MULTIDIMENSIONAL SCALING OF PERCEIVED ODOUR USING STRUCTURALLY RELATED ODORANTS

A thesis presented to the
Department of Psychology and Sociology
University of Canterbury

In fulfilment of the requirements for
the Degree of Doctor of Philosophy

by

Rodney Grant Paddick

March 1978

ABSTRACT

A series of experiments was carried out to investigate the perception of some structurally related odorants, derivatives of Bornane, Norbornane and Cyclohexane. A verbal study was carried out to determine appropriate response scale labels for the odour experiments and nine scale labels were chosen; pleasant, minty, metallic, harsh, foul, oily, resinous, sweet and camphor. Four experimental groups were chosen for the odour experiment and two groups of odours were selected, which were 18 structurally related stimuli and 5 anchor stimuli. The multidimensional scaling solutions showed 3 clusters according to core molecule type as well as regularity in the positioning of functional groups on molecules within each cluster. The anchor stimuli were well spread, as expected, due to the variation in odour type within the group. Both intra- and inter-group reliability were shown to be good for the different experimental groups. The results were discussed in respect to some of the major odour theories.

ACKNOWLEDGEMENTS

The author wishes to thank Professor R.A.M. Gregson and Dr J.M. Coxon for their guidance and assistance in the supervision of this thesis. In addition thanks are offered to Dr M.B. Simmonds for his assistance with some parts of this work.

Thanks are also due to members of the technical staff in the Psychology and Chemistry Departments, University of Canterbury, without whose assistance much of the practical work of this thesis would not have been possible.

Further thanks are due to Mrs W. van der Goot for the careful typing of this thesis.

Special thanks to my wife Jaki for her support and encouragement throughout this work.

CONTENTS

CHAPTER ONE

INTRODUCTION

This thesis is concerned with an investigation of some of the relations between chemical structure and perceived olfactory quality. There is extensive literature dealing with this topic and some will be considered here. No attempt will be made to provide an exhaustive literature survey; however an outline of some of the major experimental approaches is presented in order to place this thesis in context.

I. MOLECULAR PARAMETERS IN ODOUR PERCEPTION

Beets (1957, 1975) noted that the molecular structure of a stimulant completely defines the nature of a chemoreceptor response in a given organism under a given set of conditions. The interaction between the stimulant, which has given physical, chemical and physiological characteristics, and the organism gives rise to a chemoreceptor response.

A number of psychometric problems are associated with the interaction between physical, chemical and physiological variables and the psychological variables of the organism. Such factors as the attitude and motivation of the subject, psychological errors in judgement, the relationship between stimulus and perception

and adaptation all influence response to stimuli (Amerine, 1965).

A subject's attitude may be shown to influence the acceptance of and preference for particular stimuli. Motivation can influence threshold determinations. Psychological errors in judgement can result from numerous causes including: habituation (where there is a tendence to continue to give the same response to a slowly increasing or decreasing concentration), expectation (where the observer may find differences where none exist, if differences are expected), central tendency (where raters hesitate to use extreme values on a scale), and association (where there is a tendency to repeat previous impressions, a form of conditioned response). The presentation of different instructions or different response scales to subjects have been shown to result in different relationships between stimulus and perception (Gregson, 1962).

Adaptation occurs where a sensory system is exposed to a stimulus and there follows a temporary decrease in the sensitivity of that system. Olfactory adaptation is well known to anyone who may have walked into a room and been overwhelmed by an odour, but subsequently the observer's sensitivity is decreased and after a few minutes in that room the odour is undetectable (Köster, 1971).

In any consideration of the action of molecular structure in olfactory perception it is necessary to

consider psychometric variables present.

A variety of attempts has been made to link measurable molecular parameters with perceived odour qualities, and some of the most frequently cited will be considered here. Such variables as molecular size and shape (Amoore, Davies, Klopping), molecular vibrations measured in the infra-red and raman spectra (Wright), "profile" at the polar site (Beets, Davies, Klopping), functionality (chemical) (Beets), "polarity" of the molecule (Davies) and "intermolecular interaction forces" (Dravnieks and Laffort) have all been proposed as major determinants of perceived olfactory quality. A brief coverage of the theories proposed by each of the above mentioned workers will be given.

Amoore's "stereochemical theory" is perhaps the most often quoted and best known of the theories relating chemical structure and olfactory quality (Amoore, 1962, 1964, 1970, Amoore and Venstrom, 1965, Amoore, Johnston and Rubin, 1964).

Amoore began his work when he surveyed the literature and made lists of pure compounds with known chemical structure, all possessing the same reported smell. His initial list was reduced to seven separate classifications; camphoraceous, ethereal, musky, floral, minty, pungent, and putrid. He then went on to study the molecular structure of compounds within each of these descriptive groups.

After examination of structural formulae and mole-

cular models he suggested that odorant molecules could be arbitrarily divided into three types. These were based on the degree of confidence in assigning to the molecules a single spatial configuration. The most rigid molecules were described as "invariant", those molecules where there was conformational mobility about one or two bonds were described as "determinant" and those molecules with almost complete conformational freedom were described as "articulate". Considering mainly the "invariant" molecule types, Amoore concluded that perceived similarity of odour is associated with similarity of molecular size and shape, for any two odourants.

In his initial studies Amoore determined the shape of molecules by use of silhouette photographs of the appropriate molecular model. Atoms used for these models were manufactured by Catalin Ltd. and were said to have correct scale bond lengths,bond angles and van der Waals contact radii. The molecular models were of the "space filling" type. Amoore (1970) refers to this method as follows:

"It must be admitted that up to this stage my thesis of concordance between molecular shape and odour type had been merely intuitively apparent."

Amoore went on to use three further methods to estimate molecular shape;"(i) in the 'site-fitting method' scale models the hypothetical receptor sites were constructed and the 'goodness' of fit of the molecular model

into the site was estimated by Archimedes' principle. (ii) In the 'manual radius method' the similarity between molecular silhouette photographs was measured by comparing the corresponding radii from the centre of gravity of the silhouette to its periphery. (iii) In 'Palmieri's P.A.P.A. intersection method' the silhouette negatives were scanned by random lines generated in a television camera linked to a computer which calculated the similarity between each test silhouette and a given standard silhouette."

Amoore appears to use the terms shape and size interchangeably and his methods for defining these terms are limited. His "intuition" is limited by his apparent inability to adequately understand the molecular model. His reduction of shape into volume also seems unsound since an infinite number of different shapes can have the same volume.

In the manual radius method a single value was achieved for each pair of compounds. This was referred to as the "pseudo-vectorial difference in molecular radius ($\bar{\Delta}$)" (Amoore and Venstrom, 1967), and is a drastic oversimplification. The 'P.A.P.A. method' is a variation on the manual radius method using more sophisticated techniques but with the same effect or purpose, i.e. the reduction of size and shape to a single value.

Amoore went on to suggest that there were "Primary Odours", which were representative of each of seven major odour groups. Receptor sites were specific for each of the primary odours. Amoore's seven primary odours were: ethereal, camphoraceous, musky, floral, minty, pungent,

and putrid. Of these seven, Amoore concluded that "two were dependent not upon the size and shape of the molecules but upon their electronic states." That is, the electrophilic (electron attracting) or nucleophilic (electron donating) ability of the odorant was said to be a determining factor for olfactory quality in these two groups.

Attempts were then made to describe hypothetical receptor sites for each of the primary odours. For example, camphoraceous molecules were thought to require an oval basin-shaped receptor site, 9 Å long, 7.5 Å wide and 4 Å deep.

In one of Amoore's studies subjects performed an intensity ranking task on odorants in order to select stimuli of equal perceived intensity for quality judgement experiments. Amoore then employed the matching standards method for characterizing odour qualities (Schutz, 1964). Subjects were presented with standard odours (intensity matched primary odours) and "unknown" odours were then rated for their pair-wise similarity to each of these standards in turn. An odour dimensional analysis was then carried out and Amoore claimed that the data supported his theory.

Additional support for Amoore's theory has resulted from investigations of specific anosmia or "odour blindness". Guillot (1948) suggested that odour blindness was due to the affected person lacking one of the primary

odour detectors. Some people, having otherwise normal smell detection, fail to perceive the odour of one particular compound or group of geometrically related compounds, suggesting that the functioning of a particular receptor site is impaired (Amoore, 1970). Complex odours were said to result from concurrent stimulation of two or more primary receptor sites (Amoore, 1970; Johnston, 1963).

As a result of investigations of specific anosmia to isobutyric acid and related compounds Amoore added "sweaty" to his list of primary odours (Amoore, 1968a, 1970), and went on to suggest that there were perhaps as many as twenty or thirty primary odours.

Amoore (1968, cited in Klopping, 1971) has also acknowledged that specific functional groups may also influence the quality odour.

Klopping (1971) refers to Amoore's theory as follows:

"... in recent years Amoore has de-emphasised the site fitting concept and has stated that his original seven odour classes are not proven primary odours."

In reworking the data of Amoore and Venstrom (1965), Gregson noted the importance that molecular shape would have in any account of the psychophysics of odour similarity. However, he said that the agreement between molecular shape and odour is blurred and the distinctiveness of the primary reference odours open to question (Gregson, 1975).

Gregson has also expressed concern at the small number of subjects and the small number of observations per stimulus used in Amoore's major studies.

Amoore's selection of a wide range of odorants allows for separation into groups which have common size and shape characteristics. The use of structurally related odorants may assist the study of relations between odorants within these groups.

Wright is of the opinion that substances with similar odours should have similar low frequency vibrations. This is a modification of the work of Dyson (1926, 1928 a, b, c, d, 1929 a, b, 1931, 1938) who studied the infrared vibrations, in the 1500-3000 cm^{-1} region, of a number of structurally related compounds (mustard oils). Wright correctly observed that such vibrations are associated with the presence of specific functional groups, so in effect the correlation was with the presence or absence of a specific functional group.

Wright then concluded that skeletal vibrations of the whole molecule are the major determining factor in odour perception. He chose compounds which were rated as having similar odour to each other and observed the Raman and Infrared spectra over the wavelength range 50-700 cm^{-1}. This range was chosen after consideration of quantum requirements as follows:

Wright (1964): "... molecular vibrations are quantized, and ... a molecular vibration must have at

least one quantum of energy or else remain inactive. In general, there are only a few sources from which a molecule can draw this energy. In a flame it can come from the chemical energy of reaction - but there are no flames in the nose. Outside of a flame but within sight of it, the molecule can receive its energy by radiation - but it is dark inside the nose, so that radiative excitation of the vibrations of the odourous molecules is also ruled out. This leaves only one source of energy to excite the vibrations of the molecule, and that is the collisions it makes with the nitrogen and oxygen molecules of the air.

"Now the violence of these inter-molecular collisions is directly related to the absolute temperature, and under conditions as they exist in the nose, this is not far from 30° to 35°C, or, say, an absolute temperature of about 300°K. This is a relatively low temperature so that there is not a great amount of energy available to activate the vibrational movements, and therefore only the low-energy vibrations can be set going by collision. The size of a quantum of vibrational energy is given by $h\nu$, and so a small energy means a small value of ν (that is, a low frequency), and *vice versa*. In 1953, I calculated the average number of quanta of vibrational energy that could be given to vibrators of various frequencies by collisions with air molecules at 300°K, with the following results:

Wave number frequency	Average number of vibrational quanta per molecule
1000	0.008
800	0.022
600	0.059
400	0.17
200	0.62
100	1.62
50	3.69

"This shows that with molecules having a vibrational frequency corresponding to 1000 wave numbers, only one molecule in every 125 will be vibrating and the remaining 124 will be 'silent' (because 1/125 = 0.008). At 400 wave numbers, the proportion of vibrationally active molecules is 1 in 6, and not until the frequency is well under 200 wave numbers does each molecule have on the average one quantum of vibrational energy.

"Evidently, then, only the frequencies below about 500 wave numbers are appreciably activated by collisions with air molecules at 300^{o}K, and Dysons' 'osmic frequencies' between 1400 and 3500 wave numbers cannot possibly be right. The proper place to look for osmic frequencies is in the region between, say, 500 and 50 wave numbers."

Later, however, Wright (1966) observed: "Until now, all attempts to show that vibrations are

osmically specific have used either the observed spectroscopic frequencies or the more refined normal modes deduced from them, and these attempts have been quite unsuccessful." Wright then suggested that complex oscillations can be analysed into a finite number of vibratory motions which are mutually independent (in the absence of substantial anharmonicities) and these constitute the "normal modes" of the molecule. Each has a specific period and frequency which can be deduced from its spectra - at least in simple cases. This led him to modify his theory to include the possibility that two normal modes may be excited in the same molecule at the same time, resulting in a new frequency which is the difference between the frequencies of the normal modes. Both the difference frequencies and the normal mode frequencies were to be taken into account in his search for osmically active frequencies.

Wright and Robson (1969) also noted that not all the molecular vibrational movements are osmically active and a difference frequency that is not directly observable can be considered only if it is the difference of frequencies which are observed and known to be osmically active.

Klopping (1971) observed that these osmically active difference frequencies may not necessarily appear in the far infrared spectrum, a circumstance which would tend to render verification of Wright's theory difficult.

However, Wright ignores all cases where the difference frequency is above 650 cm^{-1}. Klopping also noted that whole molecular vibrations of molecules having the same size and shape would be expected to produce some infrared bands in common. Thus, in order to differentiate this theory from that of Amoore, it would be necessary to find molecules differing in size and shape but having similar vibrational spectra.

Of course the vibrational theory cannot explain the differences in perceived odour of certain optical isomers (Beets, 1971; Russell and Hills, 1971; Leitereg, Guadagni, Harris, Mon and Teranishi, 1971; Friedman and Miller, 1971) which would have identical raman and infrared spectra.

Further discussion of Wright's theory will be covered in Chapter VIII.

Beets (1957) proposed the "profile-functional group concept." Beets (1957, 1970) was of the opinion that the functional group of a molecule with the highest solvation* tendency is responsible for the orientation of the molecule at the receptor site. That is, polar groups are responsible for bonding with receptor sites. As a consequence of this he proposed that two structure elements are important in the perception of olfactory

* Solvation tendency and hydration tendency are used interchangeably by Beets but neither term is defined. The latter term refers to the tendency of the functional group to interact with water.

quality: the first of these being the functional group with the highest solvation tendency and the second being the profile of the rest of the molecule.

However, initial attempts to compare available data with the requirements of this model were described by Beets (1957) as "not encouraging." For example, he noted the difficulty in explaining the olfactory qualities of the nitro musks. The large number of substituents on benzene in the nitro musks causes difficulty in devising a reasonable hypothesis about their function as practically all of these musks have two or three nitro groups and the resulting orientation profiles are ambiguous.

Beets later shifted emphasis from functional groups to orientation profile as the major determinant of olfactory quality. In his 1970 paper he proposed that the orientation pattern for rigid, polar molecules, possessing a sterically accessible functional group can be expected to be homogeneous. These molecules would exist mainly in a single orientation dictated by their own polarity and by that of the receptor sites. Extensive research, concerned mainly with different types of musks, lent some support to these proposals.

In recent review articles, Beets (1971, 1973, 1975) suggested that the major criterion in determining the olfactory quality response is the shape of the oriented molecule as it is presented at the epithelium. He also

noted that the presence of a functional group is an essential characteristic of odorant quality. Other factors which Beets considers important are the steric characteristics (shape and size) of the accommodating site, the molecular profile of the odorant, and the time taken for the interaction.

It should be noted that this theory does not differ markedly from that of Amoore and much that has been said of Amoore's work is applicable here. Although Amoore only mentions that the functional group may be a factor in olfactory perception, Beets' theory makes a direct attempt to include the functional group in the proposed theoretical framework.

Davies (1953, 1965, 1970) proposed a "penetration and puncturing" theory of olfactory stimulation where stimulation was said to occur when one or more odorant molecules desorb from the lipid cell membrane. A sharp hole would then remain if the desorption time were short relative to the membrane recovery time. Davies suggested that Na^+ and K^+ ions may then interchange through this gap, initiating the nervous impulse.

Davies then proposed a range of lipid properties and molecular properties of the odorant molecules, which, in conjunction, could be responsible for different odour qualities.

The geometry of the odorant was said to be important. This includes the size of the molecule and the

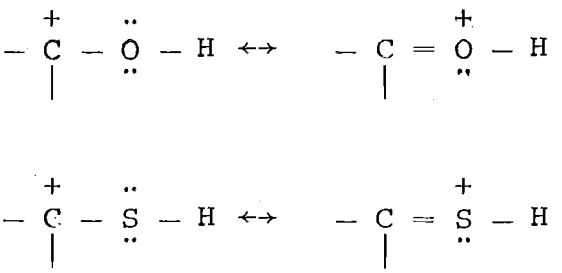
balance between its non-polar and polar portions. Another major determinant of odour quality was the cross-sectional area of the odorant. Davies and Taylor (1957) plotted molecular cross-sectional area versus energy of desorption from the lipid-water interface and showed that areas of the graph were populated by odours having particular odour qualities (For example: floral, musk and camphoraceous).

A number of properties were proposed which affected the time taken for the membrane to "heal", and hence the time available for Na^+/K^+ ion transfer. These properties included the surface pressure, rigidity and viscosity of the lipid film.

The theory gives a plausible explanation of the range of olfactory thresholds, in that different lipid layer characteristics and different molecular characteristics of odorants would require different concentrations of odorants to activate the impulses in the olfactory nerves. However, the supporting evidence for Davies' explanation of odour quality determinants is scant.

Klopping (1971) was concerned that several inconsistencies occur in the existing theories of olfactory perception. He attempted to explain the odours of small molecules (e.g. H_2S, NH_3) by introducing the concept of "inherent functional group odour" and further he has tried to relate the specific odours of certain functional groups to their electronic properties.

For example, in comparing the oxygen and sulphur groups shown below, both can readily stabilize an adjacent electron deficient centre by releasing electrons.



The hydrogen atom attached to the carbon adjacent to a sulphide group is considerably more acidic than an α-hydrogen in the corresponding ether (Price and Oae, 1962). These properties could result in different characteristic odours for the two functional groups.

Klopping concluded that:

"... in the vast majority of odorants the odour quality observed appears to be the outcome of a complicated interplay of at least three factors, e.g. size-shape, orientation with respect to the receptor surface and inherent functional group odour." Klopping suggests that the influence of one of these factors may dominate in specific instances, for example the size and shape factor is likely to become more important as the molecular size increases.

Dravnieks and Laffort (1972 and included references) suggested that there were four factors important in deter-

mining the strength of intermolecular interaction forces between the substrate and the receptor site;

(i) apolar factor (relating to van der Waals forces and proportional to the "mol volume").

(ii) proton receptor factor,

(iii) electron factor (high in unsaturated hydrocarbons) and (iv) proton donor factor (high in alcohols and primary amines).

These factors were said to be important to both quantitative and qualitative odour discrimination. Dravnieks and Laffort even claimed that these four factors were all that was required to determine odour intensity. However, complex non-linear models were found to be necessary in the discrimination of odour quality.

In spite of these efforts to establish a workable theory relating olfactory quality to chemical structure, the prediction of olfactory quality from the physicochemical properties of a wide range of substances is a study still in its infancy, which to date has been hindered by what appears to be a very limited understanding of the molecular model and the relevance of physical measurements.

II. STUDIES OF OLFACTORY PERCEPTION WHICH UTILISE SYSTEMATIC CHANGES IN MOLECULAR STRUCTURE.

There have been two basic approaches in the research in this area. The usual approach has been the investigation of a large number of differing odours and subsequent search for common molecular features of those compounds judged to be alike in some manner.

A second approach has been to examine the odour of a chemical series with a systematic change in structure. Attempts are then made to relate the physical variables to those of olfactory quality. The use of this type of stimulus series has the advantage of lowering the possible number of physicochemical variables operating in any one situation. However, such studies are generally limited to a smaller range of compounds.

In 1929 von Braun and co-workers studied the following isomeric ketones:

Methyl nonyl ketone	C_9H_{19} CO C H_3
Ethyl actyl ketone	C_8H_{17} CO C_2H_5
Propyl heptyl ketone	C_7H_{15} CO C_3H_7
Butyl hexyl ketone	C_6H_{13} CO C_4H_9
Diamyl ketone	C_5H_{11} CO C_5H_{11}

They found that as one descends the table the rue-like odour diminishes progressively and is replaced by a

fruity odour which increases progressively. Evidently the heaviest allyl group radicle in the ketone largely determines its odour (Moncrieff, 1967). For these isomeric ketones it was possible to account for the changes in odour more meaningfully than would be the case if the structure of compounds were more dissimilar.

The effect of positional isomerism in the benzene ring on the odour has been examined in some detail by Dyson (1926, 1928 a-d, 1931, 1938). He began with phenylcarbamide (phenyl mustard oil) and examined the effect on odour on the introduction of functional groups in the 2, 3 or 4 positions of the benzene ring. Substitution in the 3 (meta) position enhanced the pungency of the mustard oil odour while substitution in the 4 (para) position produced a sweet anise odour. Substitution in the 2 (ortho) position resulted in both a floral sweetness and a pungent odour, an effect that was found to be independent of the nature of the substituent. For example, replacement of a methyl substituent with halogen had no measurable effect on perceived odour.

Some work was also done with disubstituted phenyl mustard oils. It was found, however, that a chloro-substituent is more powerful than the methyl-substituent in determining the odour of the phenyl mustard oils. Studies using the chloro- and the methoxy-substituent groups were not as predictable, however, and no simple generalization is apparent in this case.

Both von Braun and Dyson used qualitative judgements (rue-like, anise, pungent, etc.) to assess the olfactory stimuli. They make no mention of how these ratings were achieved, nor how many subjects assessed the odours in order to achieve them. Caution must be exercised in the interpretation of results from such studies. For example, disparities between Japanese and American studies of qualitative perception in odour have been reported.

In von Braun's study flexible molecules were considered but no consideration was given to possible variations in molecular profile and overall shape known to be possible in such molecules.

More recently a number of researchers have studied an homologous series of aliphatic alcohols having chain length C_n, where n = 1 or 2 to n = 10 (von Braun, 1937; Engen, 1965; Mitchell and Gregson, 1968; Døving, 1970). In most cases these studies have been primarily concerned with psychophysical scaling and have not relied on verbal judgements of quality to interrelate the homologous series. Døving (1970) was of the opinion that variation in only one or two physical parameters was sufficient to determine the relation between these alcohols.

Functional groups have repeatedly shown a definite influence on the quality and intensity of odour in homologous series (McCartney, 1968).

One possible source of variation with a series

of homologous aliphatic alcohols would be the increase in conformational possibilities of the molecules with increasing chain length. In addition, vapour pressure and other physical parameters naturally change in any such homologous series. Similar problems arise in the studies of homologous series of aliphatic ketones, esters, acetates and lactones (von Braun, 1937; Stoll and Bolle, 1938; Døving, 1970).

Even for carefully chosen stimulus series as the aliphatic alcohols (or ketones, esters, etc.) there is a large number of physicochemical parameters that vary.

An interest in the problem of interpreting some of the dimensions determining the perceived olfactory quality of structurally related compounds has led to this proposed study.

III. CLASSIFICATION OF ODOUR QUALITIES

> "To be able to designate the significant characteristics of an odour by indicating which of a limited number of classes or groups it belongs would be useful for many different reasons. However, such a system must be consistent with the phenomena of odour perception, and to be effective it must be carried out with some (specifiable) degree of agreement between different people."
>
> (Harper, Bate-Smith and Land, 1968).

Many of the early systems of classification such as those of Linnaeus, Zwaardemaker or Crocker and Henderson (cited by Harper et al, 1968) consisted primar-

ily of listing odour terms and using these terms to describe and classify odours.

The number of odour terms which are used in describing odours is small. Harper et al (1968) estimate the possible range of such words to be in the order of 100 and suggested that fewer than 50 such words are practical. Even so the vocabulary is extensive to the untrained observer and the list is subject to cultural bias.

In attempts to overcome the use of verbal description in the classification of odours, McCartney (1968) quotes a number of studies which have measured physiological variables upon presentation of odours.

In such studies the choice of appropriate physiological variables is important. Studies in this field have ranged from the measurement of the salivary reflex, electro-encephalogram measures and respiration to dilation of the pupil. The measurement of these physiological variables also creates some difficulty. The standardization of measurement procedures and the reproducibility of the measurements must also be considered in the appraisal of these studies.

In addition, inappropriate data analysis may contribute to the reported difficulties in the interpretation of results in studies of this type.

Another approach which has been used is that of Amoore, grouping compounds for which certain subjects exhibit specific anosmia. Such subjects have otherwise

normal odour detection but are unable to perceive the odour of one particular compound or group of related compounds. The actual chemical identification of the specific anosmias is not as clear a procedure as, for example, might be adopted for colour vision abnormalities, and they appear to be much rarer than analogous vision defects and far less frequently presented for diagnosis. Amoore (1970) believed such a deficiency was due to one "primary odour" detector malfunction and was thus able to classify odours in this manner, all odours which are found to be related to a particular anosmia classified together.

More recent studies have utilised psychophysical scaling techniques in odour studies. These have included the use of:

1. Similarity scaling. (e.g. Gregson)
2. Semantic differential scales. (e.g. Yoshida)
3. Matching standards method. (e.g. Amoore)

Most of these studies have used metric MDS assumptions but Eyforth (1968) objected to these assumptions. However, a wide variety of studies using metric assumptions have demonstrated some consistency and partial interpretability of the MDS space (Harper et al, Yoshida, Gregson).

In most cases the psychophysical scaling techniques lead to some form of multivariate analysis. Factor analytic analyses have been quite common and cluster analyses have also been used. As multidimens-

ional scaling (MDS) has been used quite frequently in recent years with some success it would be useful to investigate this technique in more depth and consider some of the work which uses the MDS technique.

IV. MULTIDIMENSIONAL SCALING AND QUALITY OF ODOUR

In contrast with unidimensional scaling (where we have a single continuum, stimuli being represented by points along a single dimension), for multidimensional scaling we have an underlying multidimensional space with stimuli being represented by points in a space of several dimensions. There are as many numbers assigned to each stimulus as there are independent dimensions in the relevant multidimensional space, each being a scalar value corresponding to a projection of a point on one of the axes (dimensions) of the space (Torgerson, 1958).

Multidimensional scaling (MDS) procedures generally involve two steps. Firstly a model is set up concerning the characteristics of the space, which relates dimensionality of the space and projections of the points on axes of the space to distances between them. In addition, it is necessary to have a theory relating distances between points to observable relations between stimuli, the restriction being that the distances are related to observations on the relative dissimilarity

of stimuli, or some other measure of proximity, such as a probability of confusing two stimuli.

The Euclidean distance model is a tractable one for MDS in many situations as it is convenient for graphical representation and it is theoretically and conceptually simple with known mathematical properties. The distance between any two points in a Euclidean space equals the square root of the sum of the squares of differences in projections over all the orthogonal axes. If p is the Minkowski parameter, the distance between two points, given $1 < p < \infty$, is defined as

$$d_{jk} = \left[\sum_{m=1}^{n} (a_{jm} - a_{km})^p \right]^{1/p} \quad j,k = 1,2,3,...$$

and when p = 2 then we have the special and familiar case of Euclidean space. In Euclidean space the distance between points is invariant over translation and orthogonal rotation of the axes.

In contrast to the Euclidean model, the City Block model (Attneave, 1950) has p = 1 and thus defines the distance between two points as follows:

$$d_{jk} = \sum_{m=1}^{n} |a_{jm} - a_{km}| \quad j,k = 1,2,3,...$$

That is, if we have n axes the distance d_{jk} is the sum of all distances in each of the possible directions. This model is useful when the judgement of difference can be split into components (i.e. the dimensions are

psychologically obvious).

In addition to the metric models above, non-metric models of similarity have also been applied in some odour research (Mitchell, 1971) but such modelling has not been widely used in odour quality studies because MDS procedures for nonmetric similarities do not in general yet exist (Gregson, 1975).

A number of studies which used MDS in the study of odour perception have been considered in this thesis. These studies are included in Appendix I. A table summarising the experimental designs and dimensional interpretations of these studies is included here (Table I-1). Such considerations as the choice of stimuli and presentation method, method of judgement and type of rating scale, input to MDS and the type of MDS program used, are made. In addition a brief statement is made on possible interpretation of the major dimensions.

All of these studies have adopted the approach of selecting a large number of differing odours and applying MDS in the search for common features of those compounds judged to be alike.

The development of chemical series with predetermined and systematic changes for MDS analysis is quite rare. Døving (1966, 1970) reports the MDS of a series of alphatic alcohols of chain length C_3 to C_8 and refers to four other analyses on groups of six compounds or less. However, no extensive study of this

TABLE I - 1

	STIMULI USED	PRESENTATION METHOD	METHOD OF JUDGEMENT AND TYPE OF RATING SCALE	METHOD OF CONVERTING RATINGS TO INPUT OF MDS	INTERPRETATION
YOSHIDA (1964)	24 varied odours selected by perfumer, Kainoshow	Solutions of odorants were used. No mention is made of the solvent.	Three parts to experiment (i) 5 point scale, 1 being most dissimilar and 5 being most similar. (ii) 7 point bipolar scale. (iii) 5 point monopolar scale.	Not noted.	6 factors extracted and three interpreted as being real. These were: (1) Resinous vs. Sweet. (2) High pitched vs. Heavy. (3) Not Clear. Interpretation of pts. (ii) and (iii) are given in text.
YOSHIDA (1972)	Two parts (i) Used 96 of 108 (Amoore + Venstrom). (ii) 21 odours used by Dravnieks.	Not recorded.	A nine point scale for part (i). "0" being least similar and "8" being most similar. Part (ii) 8 point scale chosen. "0" being no sim. and "7" being completely similar.	Three MDS models were used. Input scores grouped and averaged over subjects, then scaled onto a distance measure.	A number of solutions were determined. Torgerson's MDS yielded Dim.I - pleasantness. Dim. II-IV - unnamed. Ekman and Hayashi, Dim.I - unnamed. Dim.II - Foul, Burnt - Unsure. Dim.III - unnamed. Micko's halomodel Dim. I + IV - unnamed.
YOSHIDA (1975)	Standard Test Odours; Amoore - 7, Wright + Michels - 7, Schulz - 9, Tablag - 10 plus 36 essential oils.	Blotting paper tabs with solvent evaporated.	Similarity scale of 9 points was used, "0" being no similarity, "8" being most similar.	Distance matrices were constructed - city block and euclidean. Both Kruskal and Torgerson MDS models were used.	Torgerson's model. Dim.I - pleasant - unpleasant. Dim.II - not clear. Kruskal's model. Dim.I - hedonic. Dim.II - resinous - non-resinous. Other dims. noted but not labelled.
BERGLUND et al. (1973)	Various. Both in retention time and pleasantness. 21 odorants matched for subjective intensity.	Liquid odorants were presented on a cotton swab.	Similarity judgement on a percentage scale. "0" represents no similarity. "100" represents identity.	Similarity values were transformed into cosine values according to the vector mode of Ekman.	Different subjects were found to have different odour spaces. 8 of the 11 subjects were found to have a hedonic dimension. Individual differences were large.
SCHIFFMAN (1974)	50 stimuli as in Wright and Michels. 25 stimuly as in Woskow.	Woskow stimulus presented in wide-mouthed reagent bottles in unadulterated form.	Verbal judgements on 9 point scale (Woskow) "1" being most alike, "9" being dissimilar.	Correlation matrices from each of the studies were used directly as input to nonmetric Guttman MDS.	Dim.I and Dim.II adequate to describe data. Appears to separate on pleasant - unpleasant.
WOSKOW (1968)	25 varied odorants were used.	Presented in wide-mouthed reagent bottles in unadulterated form.	Verbal judgements on 9 point scale. "1" being most alike, "9" being dissimilar.	Data was scaled into distances by the equal appearing model. These were then converted to a matric of scalar products using Torgerson's formula.	Dim.I - pleasantness. Dim.II - coolness or woodiness. Dim.III - unnamed.
GREGSON AND MITCHELL (1974)	Seven diverse odours.	Presented in stoppered reagent bottles as liquids (unadulterated)	Pairwise similarity judgements were made with use of an 11 point scale. "0" being completely different, "10" being identical.	INDSCAL program was used (each subjects mean ratings used as raw data).	No dimension labelling was attempted. 3 Dimensional solution accounts for 56% of the variance.

type has been found by this author. Interest in this experimental approach led to the present study.

V. THIS STUDY

For the purposes of this study a series of compounds has been chosen which have the following characteristics:

(i) Are odiferous under normal temperature and pressure conditions to most observers.
(ii) Have rigid molecular skeletons.
(iii) Have a variety of functional groups.
(iv) Have a molecular weight and an overall size that do not vary markedly within the series.

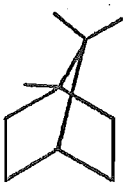
The study includes the compounds listed numbers 1 to 6 (Table I-2) which are related to camphor and the compounds numbered 7 to 12 which are derivatives of norbornane.

In order to study the effect of optical isomerism on odour, several pairs of optical enantiomers have been included in a pilot study (Numbers 2, 2(a), 3, 3(a) and 5, 5(a). See Chapter III).

The pilot study (Chapter III) was designed to determine the sensitivity of this experimental technique

Table I-2

Compounds prepared for this study



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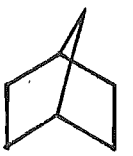

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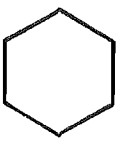

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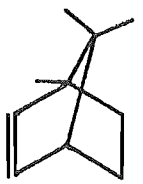

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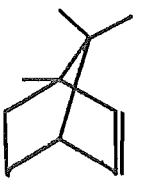
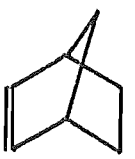


2a



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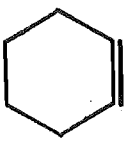

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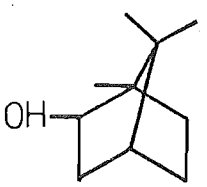

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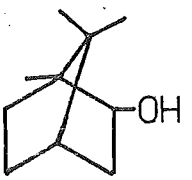
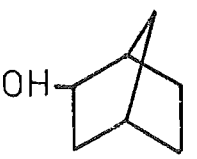


3a



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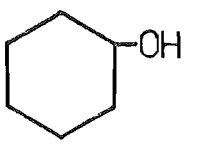

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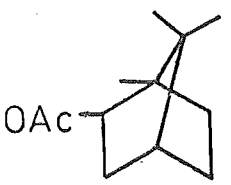

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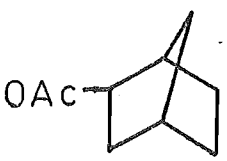

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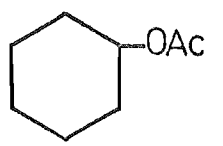

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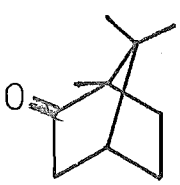

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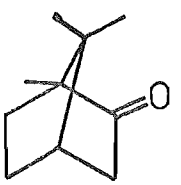

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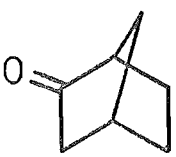

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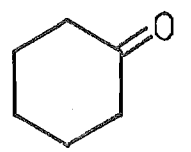

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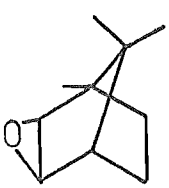

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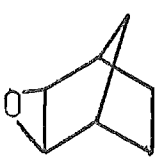

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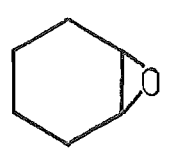


18

for the separation of the perceived odours of the chosen optical isomers. The separation was found to be small so this aspect was excluded from later studies.

As a result of this initial investigation the series of camphor related compounds (Numbers 1 to 6, Table I-2) were optically active D-isomers (with the exception of bornane which is not able to be prepared in an optically active form). The norbornane derivatives were prepared as racemic mixtures (Table I-2).

The compounds 1 to 12 are all derivatives of bicyclo[2.2.1]heptane and these were compared with a series of cyclohexane (Table I-2) and cyclopentane derivatives. Such a comparison should allow comment to be made on both the skeletal and functional group characteristics of the molecules.

The cyclohexyl and cyclopentyl compounds are not rigid in contrast with the bicycles [2.2.1] heptane derivatives. However, conformational freedom of the cyclopentyl and cyclohexyl systems is markedly less than for aliphatic derivatives. The inclusion of the cyclohexyl derivatives in this study is further justified since compound 15 (cyclohexanol), has been included in the camphoraceous group of Amoore (1970) along with (1R,2R,4R)-isoborneol ((1R,2R,4R)-bornan-2-ol) and (1R,4R)-camphor ((1R,4R)-bornan-2-one)). The fourth group (19-24), cyclopentane derivatives, was dropped from the study due to difficulty in obtaining cyclopentene in sufficient quantity to prepare other members of the group. These are not included in Table I-2.

In addition, five reference compounds were obtained as anchors in the MDS studies. The standard reference compound for camphoraceousness (1,8 Cineole) in Amoore's classification system was included and four divergent compounds, frequently used in studies of this type, were selected from a study by Gregson and Mitchell (1974). These compounds were n-propanol, methylpropionate, eugenol and isoamylacetate (see Table I-3).

Multidimensional scaling has been chosen for the data analysis in the major study for this thesis. First, however, it was necessary to develop appropriate semantic scales for use in this analysis. Hence a verbal study (Chapter IV) was carried out in which subjects were required to judge pairwise similarities of odour words. This was used to generate an odour word space by analysis with the INDSCAL MDS program. The distribution of odour words was then used in the selection of scale labels for the major study.

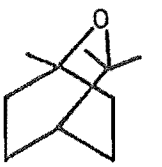
The MDS analysis used for the major study was POLYCON and Euclidean metrics were assumed in the initial analysis. Checks were then made to test the assumption of Euclidean metrics and these are discussed in Chapters V and VI. The overall results of this major study are discussed in Chapter VII.

It was also thought that additional information may have been acquired by use of a simple sorting task as outlined by Burton (1975). In such studies it has been suggested (Rosenberg and Kim, 1975) that "most

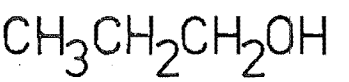
Table I-3

Anchor compounds used in this study

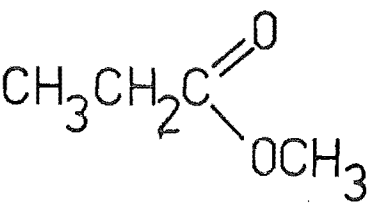
1,8-cineole



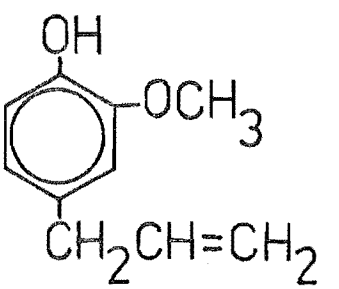
n-propanol



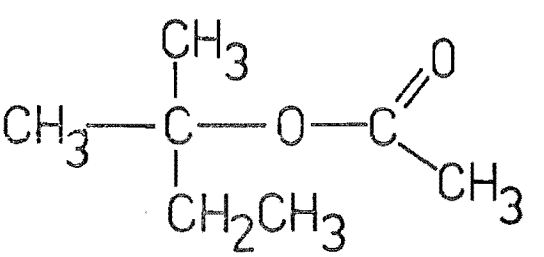
methylpropionate



eugenol



isoamylacetate



respondents ignore the most obvious dimension when they believe they only have one opportunity to indicate the dimensions in a set." For this reason a group study was selected to supplement the information gained in the major study. This study is considered in Chapter VII.

A further discussion of this study and its relation to current theory is seen in Chapter VIII.

CHAPTER TWO

SYNTHESIS

In this work we have undertaken a study of the odour of structurally related bicyclo[2.2.1]heptyl derivatives. These compounds all have a rigid skeleton which encompasses both five and six membered rings. We have therefore included in the study some cyclo, pentyl and hexyl derivatives.

The 2-substituted 1,7,7-trimethylbicyclo[2.2.1] heptyl derivatives were prepared from (1R,4R)-camphor ((1R,4R)-bornan-2-one). While some of these compounds are commercially available, the techniques required for their preparation were perfected in order to increase the efficiency of the preparations for the syntheses of the optical enantiomers from the more expensive (1S,4S)-camphor ((1S,4S)-bornan-2-one).

The 2-substituted norbornyl derivatives were prepared from norbornanone and the cyclo, pentyl and hexyl compounds from cyclopentanol and cyclohexene.

I. 2-SUBSTITUTED BORNANE DERIVATIVES

(1R,4R)-Born-2-ene was prepared by conversion of (1R,4R)-camphor to the tosylhydrazone derivative which was then reacted with methyl lithium to give (1R,4R)-

born-2-ene;

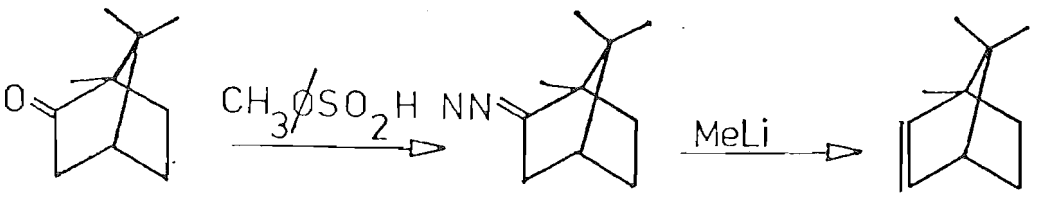


Fig. II-1

The reaction sequence provided a high yield of the alkene. The crude product was purified by vacuum distillation to give (1R,4R)-born-2-ene.

(1R,4R)-Born-2-ene was then converted to a mixture of (1R,2R,4R)-bornan-2-ol and (1S,3S,4S)-bornan-3-ol by oxymercuration-demercuration;

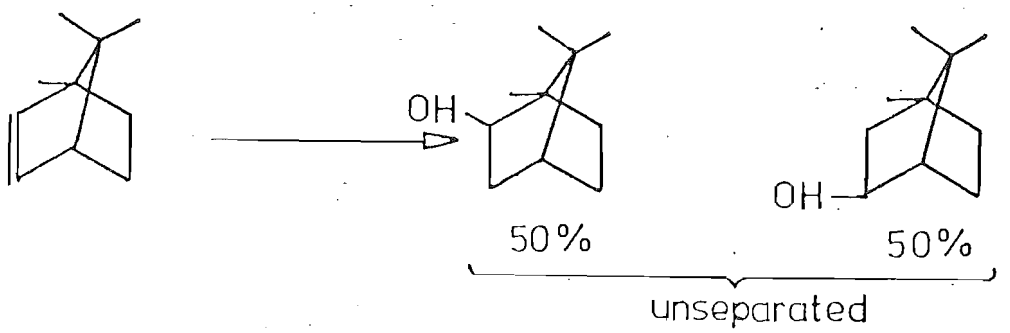


Fig. II-2

These isomers were inseparable by g.l.c. or h.p.l.c. A further attempt to separate these isomers by first converting them to their acetates [(1R,2R,4R)-born-2-yl acetate and (1S,3S,4S)-born-3-yl acetate] was also unsuccessful;

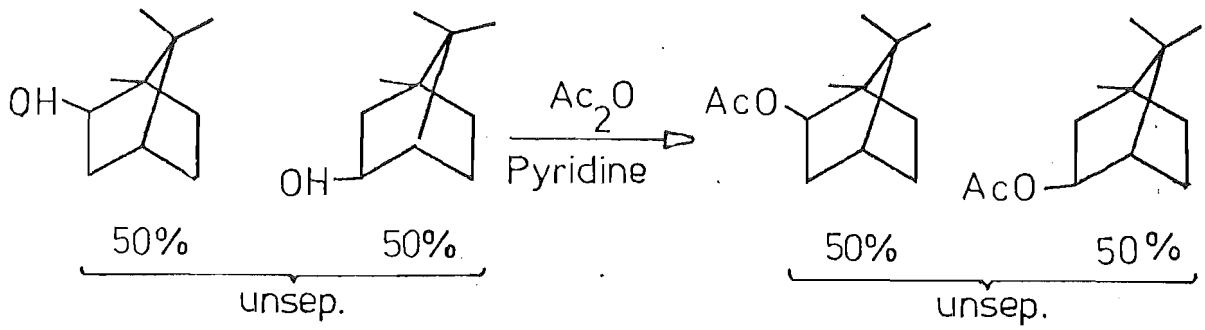


Fig. II-3

As a result of the difficulty in separating these bornane derivatives different methods of preparation were attempted in order to circumvent the problem. An alternate method of preparation of two substituted bornane derivatives was the reduction of (1R,4R)-bornan-2-one with a "mixed hydride": $LiAlH_4$ and $AlCl_3$;

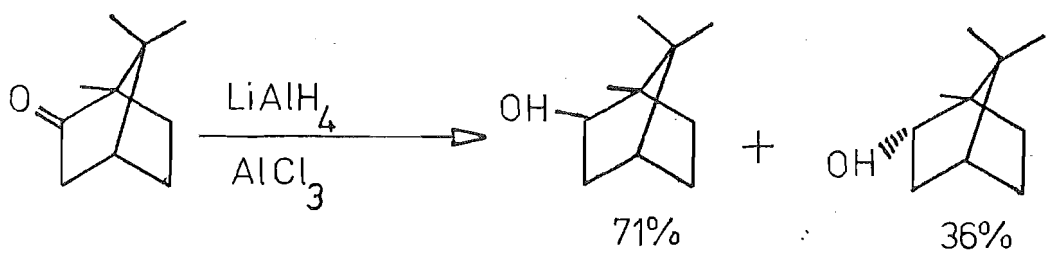


Fig. II-4

The product mixture was placed on 10% deactivated alumina and elution with pentane yielded pure (1R,2R,4R)-bornan-2-ol. Further elution with pentane yielded pure (1R,2S,4R)-bornan-2-ol.

Pure (1R,2R,4R)-bornan-2-ol was stirred with

acetic anhydride in pyridine to form (1R,2R,4R)-born-2-yl acetate;

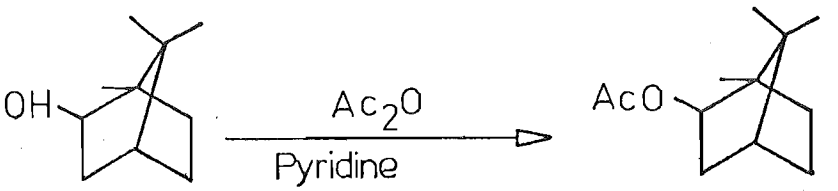


Fig. II-5

(1R,2S,4R)-Bornan-2-ol was also converted to (1R,2S,4R)-born-2-yl acetate by stirring with acetic anhydride in pyridine;

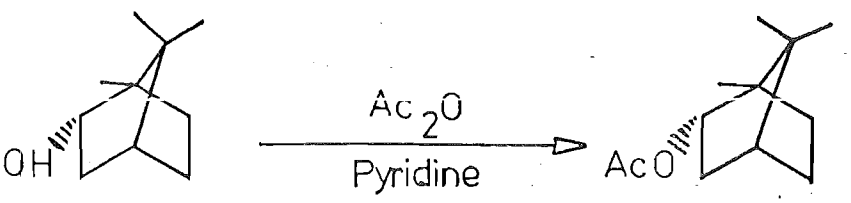


Fig. II-6

The clear oil was shown to be > 99% pure by analytical g.l.c. (1R,4R)-Born-2-ene was stirred with m-chloroperbenzoic acid and (1R,2S,3R,4S)-2,3-epoxybornane was isolated as a semisolid;

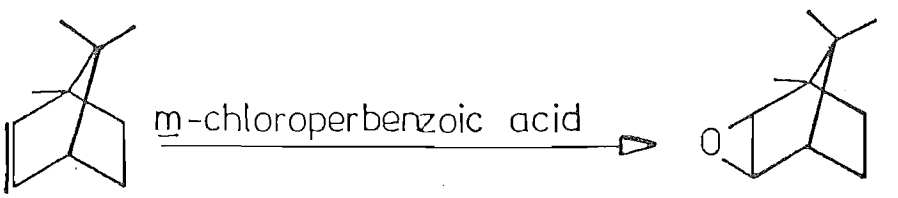


Fig. II-7

(1S,4S)-Born-2-ene was prepared by conversion of (1S,4S)-camphor to the tosylhydrazone which was then reacted with methyl lithium to form the (1S,4S)-born-2-ene;

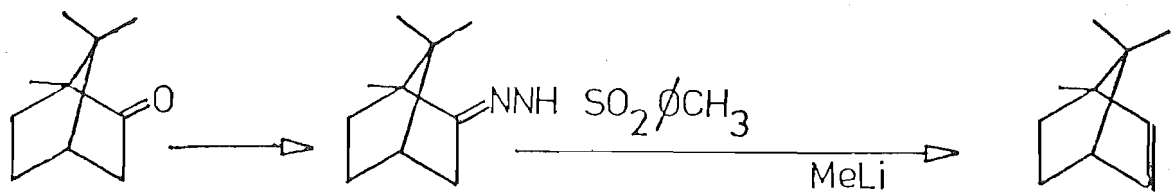


Fig. II-8

The reaction sequence provided a high yield of the alkene and the crude product was produced by vacuum distillation to give (1S,4S)-born-2-ene. (1S,4S)-Bornan-2-one was reduced in a mixed hydride solution of $LiAlH_4$ and $AlCl_3$;

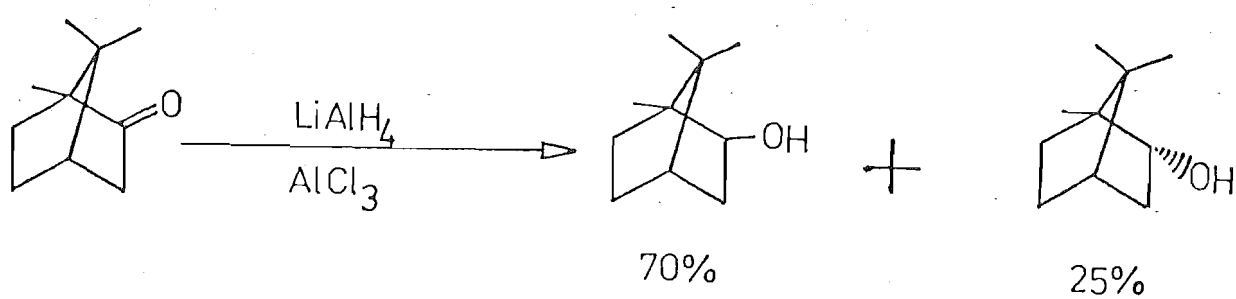


Fig. II-9

The product mixture was adsorbed onto deactivated alumina. Elution with pentane gave (1S,2S,4S)-bornan-2-ol followed by (1S,2R,4S)-bornan-2-ol.

II. 3-SUBSTITUTED BORNANE DERIVATIVES

Two attempts were made to prepare 3-substituted bornane derivatives. The first oxymercuration-demurcuration of (1R,4R)-born-2-ene has already been discussed. The second method involved (1R,4R)-camphorquinone which was treated with zinc and acetic acid to give (1R,4R)-2-hydroxyepicamphor but yields of this compound were too low for the method to be pursued.

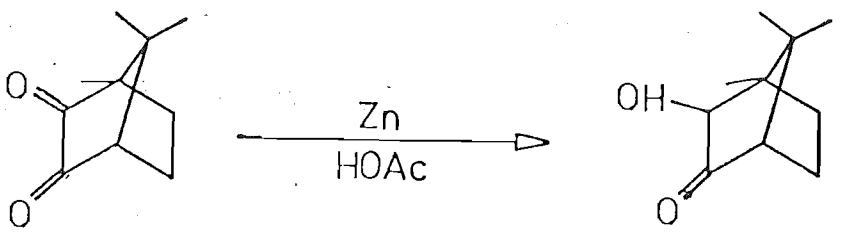


Fig. II-10

III. NORBORNANE DERIVATIVES

All norbornane derivatives were racemic mixtures. A pressure hydrogenator was used in the conversion of norbornene (bicyclo[2.2.1]hept-2-ene) to norbornane (bicyclo[2.2.1]heptane) using a Pt/carbon catalyst. The reaction mixture was stirred until H_2 uptake ceased.

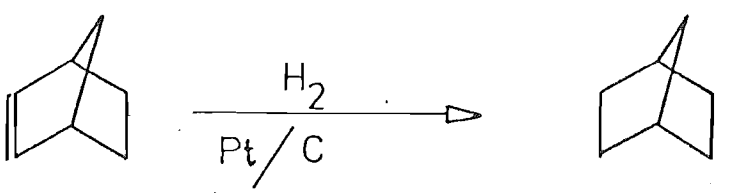


Fig. II-11

Oxymercuration-demercuration of norbornene yielded a product mixture which on reduction with $LiAlH_4$ and adsorption on alumina and elution with pentane gave exo-norborneol (exo-bicyclo[2.2.1]heptan-2-ol);

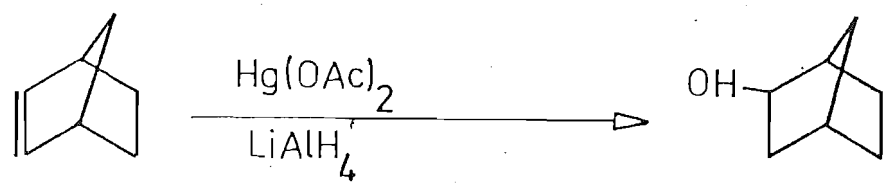


Fig. II-12

The p.m.r. spectra of the reaction mixture and column fractions suggested that endo-norborneol (endo-bicyclo [2.2.1]heptan-2-ol) was also produced but this was not isolated pure.

exo-Norborneol was stirred in acetic anhydride and pyridine to form exo-norbornyl acetate (exo-bicyclo [2.2.1]hept-2-yl acetate) as a clear oil;

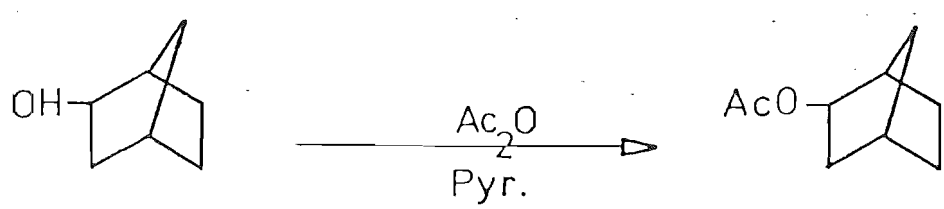


Fig. II-13

Norbornene was stirred with m-chloroperbenzoic acid to form exo-2,3-epoxynorbornane (2,3-exo-epoxybicyclo [2.2.1]heptane).

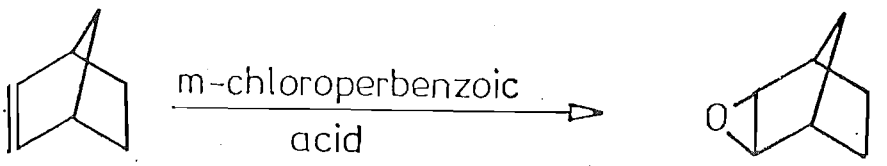


Fig. II-14.

This was formed as a white solid and was found to be greater than 99% pure by analytical g.l.c.

IV CYCLOHEXANE DERIVATIVES

Cyclohexane, cyclohexene, cyclohexanone and cyclohexanol were available commercially. Cyclohexanol was reacted with acetic anhydride in pyridine to give cyclohexyl acetate shown after distillation to be 99% pure by analytical g.l.c.

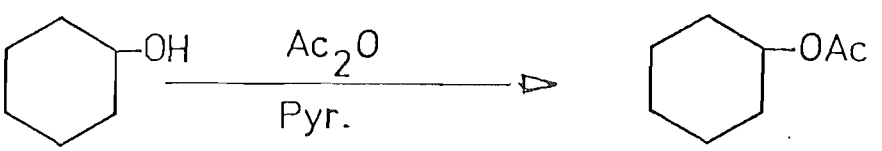


Fig. II-15.

Cyclohexene was stirred with monoperoxyphthalic acid for 24 hours to give epoxycyclohexane;

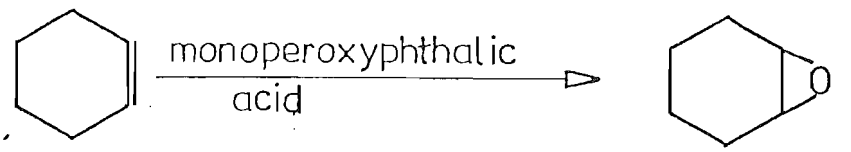


Fig. II-16.

V. CYCLOPENTANE DERIVATIVES

Only two cyclopentane derivatives were available for this study, cyclopentanone and cyclopentanol. Attempts to purchase cyclopentene were unsuccessful due to repeated breakages in shipping!

Cyclopentyl acetate was prepared in the usual way;

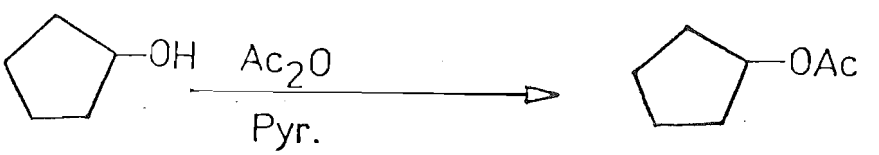


Fig. II-17.

VI. EXPERIMENTAL CHEMISTRY

In general, common names have been used to identify compounds and examples are seen in Table I-2, page 29. However, for the purposes of this section on preparative chemistry the systematic naming of these compounds has been included.

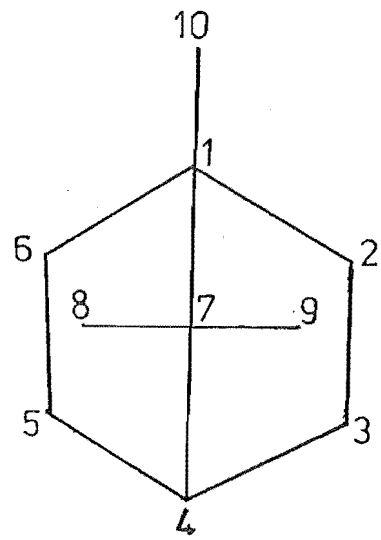
IUPAC conventions for cyclic hydrocarbons are outlined in "Definitive Rules for Nomenclature of Organic Chemistry", (IUPAC, 1960). A review of organic nomenclature has recently been published; "Nomenclature of Organic Compounds", (Fletcher, Dermer and Fox, 1973).

The parent hydrocarbons used in this work are pictured below and both common and systematic names are shown with the carbon atoms numbered in the usual way.

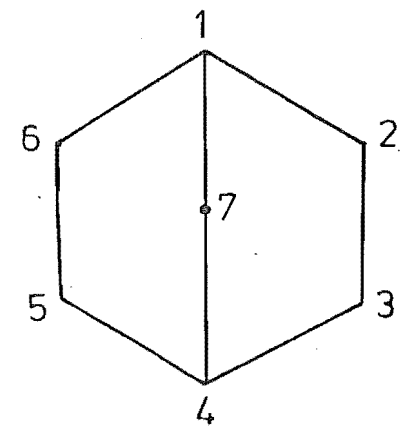
The nomenclature committee of IUPAC recommends that the use of "bornane" is preferred to "1,7,7-trimethylbicyclo[2.2.1]heptane" but for "norbornanes" the systematic name, "bicyclo[2.2.1]heptane", is preferred. Chemical Abstracts uses both naming systems when identifying norbornane derivatives.

Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer as Nujol mulls. P.m.r. spectra were recorded on a Varian T60 spectrometer in $CDCl_3$ solution with $SiMe_4$ and $CHCl_3$ as internal standards. Melting points are uncorrected and micro-analyses were performed at the University of Otago. The purity of compounds used in the olfactory experiments was determined by analytical

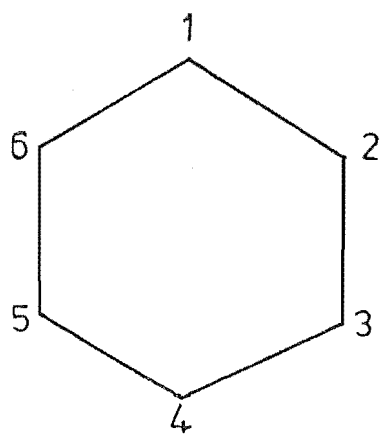
Parent Hydrocarbons used in this study:



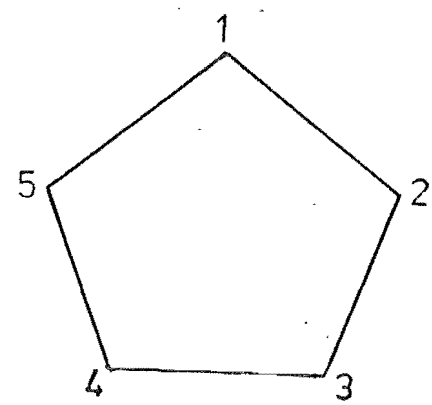
Bornane
(1,7,7-trimethylbicyclo-[2.2.1]heptane)



Norbornane
(Bicyclo[2.2.1]heptane).



Cyclohexane



Cyclopentane

Fig. II-18

g.l.c. on a Varian Aerograph 1200 with a flame ionization detector.

The alumina used for column chromatography was Grade H. Deactivated alumina refers to alumina to which 10% of a 10% solution of acetic acid has been added. The silica gel used for column chromatography was Crosfield quality grade B.S.S. Sorbsil. Solvents used for chromatography were technical grade dried with P_2O_5 and distilled. High pressure liquid chromatography (HPLC) was carried out using an alumina analytical column (3 mm by 90 cm). Where other columns were used this is indicated. Optical rotations were determined using a 1 cm quartz cell in an ETL-NPL Automatic Polarimeter.

(1R,4R)-Bornan-2-one tolylsulphonylhydrazone ((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one tolylsulphonylhydrazone)

Concentrated hydrochloric acid (2 ml) was added to a solution of (1R,4R)-bornan-2-one ((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one) (76.1 g) and tolylsulphonylhydrazide (86.1 g) in tetrahydrofuran (250 ml) and the mixture was heated under reflux for 6 hours. The tetrahydrofuran was removed by distillation. Benzene was added to the residue and removed by distillation to give (1R,4R)-bornan-2-one tolylsulphonylhydrazone (145 g) as white crystals. m.p. 115-116°C $[\alpha]_D^{27}$ 14° (c 1.05). ν_{max} 3200, 1661, 1155, 810 and 670 cm^{-1}. P.m.r.

δ 7.72 (Wh/2 16 Hz) and 7.28 (Wh/2 16 Hz, aromatic H's); 2.39, $ArCH_3$; 0.90, 0.85 and 0.50 (CH_3's). (Lewis, 1970).

Methyl lithium

Lithium (16g) was added to dry ether (400 ml) under an atmosphere of dry N_2 and the mixture cooled to below -10°. Bromomethane (100 g, 58 ml) in ether (200 ml) was slowly added with cooling over a period of 2 hours. The temperature was allowed to rise 10° and the mixture stirred for a further 2 hours. The mixture was filtered under dry N_2 to give LiMe in ether (500 ml; 1.5M).

(1R,4R)-Born-2-ene ((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene)

Crystalline (1R,4R)-bornan-2-one tolylsulphonyl-hydrazone (76.5 g) was dissolved in ether (100 ml) and stirred under an atmosphere of dry N_2 at 20°. A freshly prepared solution of LiMe in ether (300 ml; 1.5M) was added over a period of 40 min. and the reaction stirred for a further 2.5 hr. until the evolution of N_2 ceased. Water was carefully added and the product isolated by means of pentane. After removal of the solvent by distillation through a Vigreux column the product was adsorbed onto activated alumina (1 kg) and elution with pentane to give (1R,4R)-born-2-ene which was further purified by distillation. (1R,4R)-Born-2-ene; (10.7 g)

m.p. 109-110^{0}. $[\alpha]_{D}^{25}$ -20.3^{o} (c. 1.02 toluene). ν_{max} 718 cm^{-1}. P.m.r. δ 5.92 ($J_{2\text{-}H,3\text{-}H}$ 5.8 Hz, $J_{3\text{-}H,4\text{-}H}$ 0.9 Hz; $C^{3}H$); 5.66 ($J_{2\text{-}H,3\text{-}H}$ 5.8 Hz, $J_{2\text{-}H,6\text{-}\underline{exo}\text{-}H}$ 0.9 Hz; $C^{2}H$); 2.28 ($J_{4\text{-}H,3\text{-}H}$ 2.9 Hz, $C^{4}H$); 1.03 ($C^{10}H_{3}$); 0.83 ($C^{9}H_{3}$); 0.77 ($C^{8}H_{3}$). Purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. (Lewis, 1970).

Oxymercuration-demercuration of (1R,4R)-born-2-ene

Mercuric acetate (7.05 g) was added to a solution of (1R,4R)-born-2-ene (3.0 g) in aqueous tetrahydrofuran (1:1; 45 ml) and the mixture stirred to 20^{o} for 2.5 hr. Aqueous sodium hydroxide (3M, 12 ml) followed by sodium borohydride (0.5 g) in aqueous sodium hydroxide (3M 12 ml) was added and the mixture stirred at 20^{o} for 20 min. Isolation of the product by means of ether gave after removal of the solvent a semi-solid (3.08 g). The product mixture was allowed to react with lithium aluminium hydride (2 g) in dry ether (250 ml) for 1 hr. to give a mixture of (1R,2R,4R)-bornan-2-ol ((1R,2R,4R)-1,7,7-trimethylbicyclo [2.2.1]heptan-2-ol) and (1S,3S,4S)-bornan-3-ol ((1S,3S,4S)-trimethylbicyclo[2.2.1]heptan-2-ol)(1:1, 39). All attempts* to separate these isomers failed.

*Chromatography on 10% deactivated alumina or silica gel - g.l.c. on carbowax or EGA and h.p.l.c. on alumina, silica or duropak columns.

(1R,2R,4R)-Born-2-yl acetate and (1S,3S,4S)-born-3-yl acetate

A mixture of (1R,2R,4R)-bornan-2-ol and (1S,3S,4S)-bornan-3-ol (2.5 g), pyridine (100 ml) and acetic anhydride (20 ml) was kept at room temperature for 18 hr. The mixture was poured into ether and washed with dilute sulphuric acid (10x) and aqueous sodium bicarbonate (5x). The organic phase was dried with anhydrous magnesium sulphate and after removal of solvent gave a mixture of (1R,2R,4R)-born-2-yl acetate ((1R,2R,4R)-trimethylbicyclo [2.2.1]hept-2-yl acetate) and (1S,3S,4S)-born-3-yl acetate ((1S,3S,4S-trimethylbicyclo[2.2.1]hept-3-yl acetate). P.m.r. δ 2.00 (OAc); 1.98 (OAc). All attempts to separate this mixture failed.

Reduction of (1R,4R)-bornan-2-one

To a cooled "mixed hydride" solution, prepared by addition of lithium aluminium hydride (20 ml; 1M) in ether to aluminium chloride (10 g) in ether (80 ml), was added (1R,4R)-bornan-2-one (10 g) in ether (50 ml) over a period of 30 min. The solution was stirred at room temperature for 1 hr. Hydrated sodium sulphate was added followed by the careful addition of a few drops of water. The organic phase was dried with anhydrous magnesium sulphate and after removal of solvent gave (1R,2R,4R)-bornan-2-ol (71%) ((1R,2R,4R)trimethylbicyclo[2.2.1]heptan-2-ol), (1R,2S,4R)-bornan-2-ol ((1R,2S,4R)-trimethylbicyclo[2.2.1]heptan-2-ol) (26%) and camphene (3%).

The product mixture was adsorbed onto deactivated alumina. Elution with pentane gave pure samples of (1R,2R,4R)-bornan-2-ol (1 g) and (1R,2S,4R)-bornan-2-ol (0.1 g). Chromatography was repeated on the mixed fractions to give (1R,2S,4R)-bornan-2-ol (1 g).

(1R,2R,4R)-Bornan-2-ol; m.p. 207-208^{o}, $[\alpha]_{D}^{20}$ - 19^{o} (c 1.00 toluene). ν_{max} 3616 cm^{-1}. P.m.r. δ 3.62 ($J_{2\text{-}\underline{endo}\text{-H},\ 3\text{-}\underline{endo}\text{-H}}$ 6.7 Hz, $J_{2\text{-}\underline{endo}\text{-H},\ 3\text{-}\underline{exo}\text{-H}}$ 4.2 Hz; C^{2}-$\underline{endo}$-H); 1.2 ($C^{8}H_{3}$); 0.90 ($C^{10}H_{3}$); 0.82 ppm ($C^{9}H_{3}$). This compound was shown to be greater than 99% pure by analytical g.l.c. using a carbowax column. Micro-analysis: C, 77.84 (77.94)%; H 11.75 (11.68)%. (Lewis, 1970).

(1R,2S,4R)-Bornan-2-ol; m.p. 204-206^{o}. ν_{max} 3230 and 1050 cm^{-1}. P.m.r. δ 4.00 ($J_{2\text{-}\underline{exo}\text{-H},\ 3\text{-}\underline{exo}\text{-H}}$ 11.0 Hz, $J_{2\text{-}\underline{exo}\text{-H},\ 3\text{-}\underline{endo}\text{-H}}$ 4.0 Hz, $J_{2\text{-}\underline{exo}\text{-H},\ 6\text{-}\underline{exo}\text{-H}}$ 2.0 Hz; C^{2}-$\underline{exo}$-H); 0.86 ppm ($C^{8}H_{3}$, $C^{9}H_{3}$, $C^{10}H_{3}$). Purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. Micro-analysis: C, 77.78 (77.94)%, H, 11.89 (11.68)%.

(1R,2R,4R)-Born-2-yl acetate

Acetic anhydride (20 ml) was added to a solution of (1R,2R,4R)-bornan-2-ol (2.5 g) in pyridine (100 ml) and the solution stirred at 20^{o} for 27 hr. The product was isolated by means of ether and after removal of solvent gave (1R,2R,4R)-born-2-yl acetate (1.13 g) as an oil. ν_{max} 1730 and 1240 cm^{-1}. P.m.r. 4.68 ($J_{2\text{-}\underline{endo}\text{-H},\ 3\text{-}\underline{endo}\text{-H}}$

5.7 Hz, J_{2}-endo-H, 3-exo-H 5.7 Hz; C^{2}-endo-H); 2.00 (OAc); 0.98 ($C^{8}H_{3}$); 0.84 ppm ($C^{9}H_{3}$ and $C^{10}H_{3}$). The purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. Microanalysis: C, 74.66 (73.49) %; H, 10.15 (10.20)%.

(1R,2S,4R)-Born-2-yl acetate. ((1R,2S,4R)-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl acetate)

Acetic anhydride (20 ml) was added to a solution of (1R,2S,4R)-bornan-2-ol (2.5 g) in pyridine (100 ml) and the solution stirred at 20° for 27 hr. Isolation by means of ether and distillation of the crude product gave (1R,2S,4R)-born-2-yl acetate (1.10 g) as an oil. ν_{max} 1740 and 1235 cm^{-1}. P.m.r. δ 4.90 (J_{2}-exo-H, 3-exo-H 11.0 Hz, J_{2}-exo-H, 3-endo-H 4.0 Hz, J_{2}-exo-H, 6-exo-H 2.5 C^{2}-exo-H); 2.05 (OAc), 0.90 and 0.86 ($C^{8}H_{3}$, $C^{9}H_{3}$, $C^{10}H_{3}$). Purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column.

(1R,2S,3R,4S)-2,3-Epoxybornane ((1R,2S,3R,4S)-2,3-epoxy-1,7,7trimethylbicyclo[2.2.1]heptane

meta Chloroperbenzoic acid (3.74 g) was added to a solution of (1R,4R)-born-2-ene (3.0 g) in ether (20 ml) and the mixture was stirred for seven days. The organic phase was washed with dilute sodium hydroxide, water and dried with anhydrous magnesium sulphate. The solvent

was removed by careful distillation to give (1R,2S,3R, 4S)-2,3-epoxybornane (2.95 g) as a semi-solid. ν_{max} 1730 and 860 cm^{-1}. P.m.r. δ 3.52 ($J_{3\text{-}\underline{exo}\text{-}H,\ 2\text{-}\underline{exo}\text{-}H}$ 4 Hz, $J_{3\text{-}\underline{exo}\text{-}H,4H}$ 4 Hz, C^3H); 3.20 ($J_{2\text{-}\underline{exo}\text{-}H,\ 3\text{-}\underline{exo}\text{-}H}$ 4 Hz, C^2H); 1.05, 0.93, 0.75 (CH_3's).

(1S,4S)-Bornan-2-one tolylsulphonylhydrazone. ((1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one tolylsulphonylhydrazone)

Concentrated hydrochloric acid (2 ml) was added to a solution of (1S,4S)-bornan-2-one ((1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one) (76.1 g) and tolylsulphonylhydrazide (86.1 g) in tetrahydrofuran (250 ml) and the mixture was heated under reflux for 6 hr. The tetrahydrofuran was then removed by distillation. Benzene was added and removed by distillation to give (1S,4S)-bornan-2-one tolylsulphonylhydrazone (145 g) as white crystals. m.p. 115-116°C. $[\alpha]_D^{27}$ -13° (c 1.05). ν_{max} 3200, 1661, 1155, 810 and 670 cm^{-1}. P.m.r. δ 7.72 (Wh/2 16 Hz) and 7.28 (Wh/2 16 Hz, aromatic H's); 2.39 ($ArC\underline{H}_3$); 0.90, 0.85 and 0.50 ppm (CH_3's).

(1S,4S)-Born-2-ene ((1S,4S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene)

Crystalline (1S,4S)-bornan-2-one tolylsulphonylhydrazone (76.5 g) was dissolved in ether (100 ml) and

stirred under an atmosphere of dry (N_2 at 20°. A freshly prepared solution of LiMe in ether (300 ml, 1.5M) was added over a period of 40 min. and the reaction stirred for a further 2.5 hr. until the evolution of N_2 ceased. Water was carefully added and the product isolated by means of pentane. After removal of the solvent by distillation through a Vigreux column, the product was adsorbed onto activated alumina (1 kg) and elution with pentane gave (1S,4S)-born-2-ene which was further purified by distillation. (1S,4S)-born-2-ene; (10.7 g). m.p. 109-110°. $[\alpha]_D^{25}$ + 19.0° (c 1.04 toluene). ν_{max} 718 cm^{-1}. P.m.r. δ 5.92 ($J_{2\text{-}H,3\text{-}H}$ 5.8 Hz, $J_{3\text{-}H,4\text{-}H}$ 0.9 Hz; C^3H; 5.66 ($J_{2\text{-}H,3\text{-}H}$ 5.8 Hz, $J_{2\text{-}H,6\text{-}\underline{exo}\text{-}H}$ 0.9 Hz; C^2H); 2.28 ($J_{4\text{-}H,3\text{-}H}$ 2.9 Hz; C^4H); 1.03 ($C^{10}H_3$); 0.83 (C^9H_3); 0.77 (C^8H_3). Purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. (Lewis, 1970).

Reduction of (1S,4S)-bornan-2-one

To a cooled "mixed hydride" solution, prepared by addition of lithium aluminium hydride (20 ml; 1M) in ether to aluminium chloride (10 g) in ether (50 ml), was added (1S,4S)-bornan-2-one (10 g) in ether (50 ml) over a period of 30 min. The solution was stirred at room temperature for 1 hr. Hydrated sodium sulphate was added followed by the careful addition of a few drops of water. The organic phase was dried with anhydrous magnesium sulphate and after removal of solvent gave (1S,2S,4S)-

bornan-2-ol (71%), (1R,2S,4R)-bornan-2-ol ((1S,2R,4S)-trimethylbicyclo[2.2.1]heptan-2-ol) (26%) and camphene (3%).

The product mixture was adsorbed onto deactivated alumina. Elution with pentane gave pure samples of (1S,2S,4S)-bornan-2-ol (0.9 g) and (1S,2R,4S)-bornan-2-ol (0.1 g). Chromatography was repeated on the mixed fractions.

(1S,2S,4S)-Bornan-2-ol; m.p. 207-208°. $[\alpha]_D^{25}$ + 19° (c 1.0 toluene). ν_{max} 3616 cm^{-1}. P.m.r. δ 3.62 ($J_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 6.7 Hz; $J_{2\text{-}\underline{endo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 4.2 Hz; C^2-$\underline{endo}$-H); 1.02 (C^8H_3); 0.90 ($C^{10}H_3$); 0.82 ppm (C^9H_3). The purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. Microanalysis: C, 77.84 (77.94)%; H, 11.75 (11.68)%. (Lewis, 1970).

(1S,2R,4S)-bornan-2-ol; m.p. 204-206°. ν_{max} 3230 and 1050 cm^{-1}. P.m.r. δ 4.00 ($J_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{exo}\text{-}H}$ 11.0 Hz, $J_{2\text{-}\underline{exo}\text{-}H,3\text{-}\underline{endo}\text{-}H}$ 4.0 Hz, $J_{2\text{-}\underline{exo}\text{-}H,6\text{-}\underline{exo}\text{-}H}$ 2.0; C^2-$\underline{exo}$-H); 0.86 ppm (C^8H_3, C^9H_3, $C^{10}H_3$). Purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. Microanalysis: C, 77.78 (77.94)%; H, 11.89 (11.68)%.

Norbornane (bicyclo[2.2.1]heptane)

A mixture of norborn-2-ene (bicyclo[2.2.1]hept-2-ene) (10 g), Pt-C catalyst (10 g) in pentane (100 ml) was stirred vigorously in a hydrogen atmosphere. After the

absorption of 1 mole equivalent of hydrogen the mixture was filtered through celite to remove the catalyst and the solvent was removed by distillation using a Vigreux column to give norbornane (10 g) as a white semi-solid. ν_{max} 1740, 1120, 990, 975, 870 and 850 cm^{-1}. P.m.r. δ 2.23 (2H, C^7H_2), 1.70-1.05 (m, 10H). Purity was determined to be greater than 99% by analytical g.l.c. using a carbowax column. Microanalysis: C 87.26 (87.51)%; H, 12.86 (12.49)%.

Oxymercuration-demercuration of norbornene.

Mercuric acetate (105 g) was added to a solution of norbornene (30 g) in aqueous tetrahydrofuran (1:1, 500 ml) and the mixture stirred at 20^{o} for 3 hours. Aqueous sodium hydroxide (3M; 180 ml) followed by sodium borohydride (6 g) in aqueous sodium hydroxide (3M; 180 ml) was added and the mixture stirred at 20^{o} for 20 min. Isolation of the product by means of ether gave after removal of the solvent a semi-solid.

The product mixture was allowed to react with lithium aluminium hydride (10 g) in dry ether (2 l) for 1 hr. to give exo-norborneol. The product was adsorbed onto alumina (10% deactivated) and elution with pentane and benzene gave exo-norborneol (exo-bicyclo [2.2.1]heptan-2-ol). ν_{max} 3350, 1350, 1070, 1000 and 910 cm^{-1}. P.m.r. δ 3.72 ($J_{2\text{-endo-H},3\text{-endo-H}}$ 6.5 Hz, $J_{2\text{-endo-H},3\text{-exo-H}}$ 2.5 Hz, $J_{2\text{-endo-H},\ 1\text{-H}}$ 2 Hz, C^2-endo-H).

Purity was determined to be greater than 99% by analytical g.l.c. Microanalysis: C, 74.81 (75.00)%; H, 10.56 (10.70)%.

Norbornyl acetate (exo-bicyclo[2.2.1]hept-2-yl acetate)

Acetic anhydride (10 ml) was added to a solution of norborneol (5 g) in pyridine (50 ml) and the solution kept at 20° for 24 hours. The reaction mixture was then poured into an ether-water mixture and the organic phase washed with dilute sulphuric acid, saturated sodium bicarbonate and with water and dried ever anhydrous magnesium sulphate. After removal of the solvent exo-norbornylacetate (∿ 5 g) was obtained as a clear oil. ν_{max} 1740, 1450, 1440, 1350, 1340, 1240, 1170 and 1110 cm^{-1}. P.m.r. δ 4.58, $J_{2\text{-endo-H},3\text{-endo-H}}$ 6.5 Hz, $J_{2\text{-endo-H},3\text{-exo-H}}$ 2.5 Hz, $J_{2\text{-endo-H}, 1\text{-H}}$ 2 Hz; C^2-endo-H). Purity was determined to be greater than 99% by analytical g.l.c.

exo-2,3-Epoxynorbornane (2,3-exo-epoxybicyclo[2.2.1] heptane)

To a solution of norbornene (3.0 g) in ether (50 ml) was added meta-chloroperbenzoic acid (6 g) and the resulting solution stirred for 4 days. The reaction mixture was poured into ether and washed ten times with aqueous sodium bicarbonate, then dried over $MgSO_4$ and

the solvent removed by distillation through Vigreux column to give exo-2,3-epoxynorbornane as a white gel (3 g). ν_{max} 1740, 1135, 1020, 990, 975, 870 and 850 cm^{-1}. P.m.r. δ 3.08 (Wh/2 3 Hz; C^2-H and C^3-H), 2.46 (Wh/2 6 Hz; C^1-H and C^4-H). The purity was found to be greater than 99% using analytical g.l.c. Microanalysis: C, 76.06 (76.36)%; H, 9.00 (9.08)%.

Cyclohexylacetate

Acetic anhydride (40 ml) was added to a solution of cyclohexanol (30 ml) in pyridine (140 ml) and the solution kept at room temperature for 24 hr. The product was isolated by means of pentane to give cyclohexylacetate (20 ml). ν_{max} 1450, 1350, 1340, 1110, 1040, 1015 and 960 cm^{-1}. P.m.r. δ 4.70 (1H); 2.00 (-OAc); 1.95-1.12 ppm (10H). Purity was determined to be greater than 99% by analytical g.l.c.

1,2-Epoxycyclohexane

To a solution of cyclohexene (2.5 g) in ether (20 ml) was added an excess of freshly prepared monoperoxyphthalic acid in ether and the mixture was stirred for 24 hours. The reaction mixture was poured into pentane and washed with dilute sodium hydroxide, water and dried over magnesium sulphate. After removal of the $MgSO_4$ the solvent was removed by distillation through a Vigreux column, to give

epoxycyclohexane (1.33 g). ν_{max} 3500, 1790, 1730, 960, 890, 840 and 780 cm^{-1}. P.m.r. δ 3.12 (Wh/2 - Hz; C^1-H and C^2-H). Purity was determined to be greater than 99% by analytical g.l.c.

Cyclopentylacetate

Acetic anhydride (10 ml) was added to a solution of cyclopentanol (10 ml) in pyridine (40 ml) and the mixture left for 24 hours at room temperature. The product was isolated by pouring into pentane and washing ten times with sodium bicarbonate solution, several times with dilute sulphuric acid and water. The product was dried over $MgSO_4$ and the solvent removed by distillation through a Vigreux column to give cyclopentylacetate (10 ml). ν_{max} 1740, 1350, 1240, 1160 and 1020 cm^{-1}. P.m.r. δ 5,20 (C^1-H); 2.00 (OAc). The purity was determined to be greater than 99% by analytical g.l.c.

CHAPTER III

PILOT STUDY

The purpose of this study was to find an appropriate method of stimulus presentation and a response scale, and to select stimuli for the major study.

Presentation of Stimuli

Stone (1963), in discussing the relative methods of the olfactometric and sniffing techniques, noted the following ...

"The sniff method is suited to study of odor quality, industrial quality control, and other investigations not involving quantitative investigation of the olfactory process, behavioral aspects, and odorimetry, for which the olfactometer is ideally suited."

The sniff procedure involves the presentation of odorous samples in flasks and the subject is required to remove the cover and inhale the vapour from the flask. The sniff method is cheap and simple. Most sniff procedures have used a diluent such as water or odour-free mineral oil (Stone, 1963; Cain, 1969).

Olfactometers have become elaborate, and are based on some quantitative air-dilution system where a known volume of odour-saturated air is diluted in a larger volume of clean air (or even nitrogen in some olfactometers).

This odour/air mixture is then presented to the subject at controlled temperature and air flow.

Calibration of an olfactometer requires knowledge of the vapour pressure of the odorant at operating temperature and the molecular volume of STP. These data are not available for some members of the present stimulus series.

It would be necessary to overcome the calibration problems encountered by the sniff bottle and/or the olfactometric presentation techniques if intensity measures were the major consideration. However, Stone (1963) has demonstrated that it is unnecessary to use olfactometric techniques for studies of qualitative variations over a series of chemically diverse compounds.

It would appear from these considerations that the sniff method is practically and economically suited to the purposes of this thesis.

Stone (1963) used a mineral oil (as used by Jones, 1955a, b) and demonstrated deviations from ideal solution behaviour. In addition, Cain (1969) noted that:

"Since there is, moreover, no liquid that is both completely odorless and an effective solvent for all odorants, dilution of the odorant in air (or another gas) is preferable to dilution in a liquid."

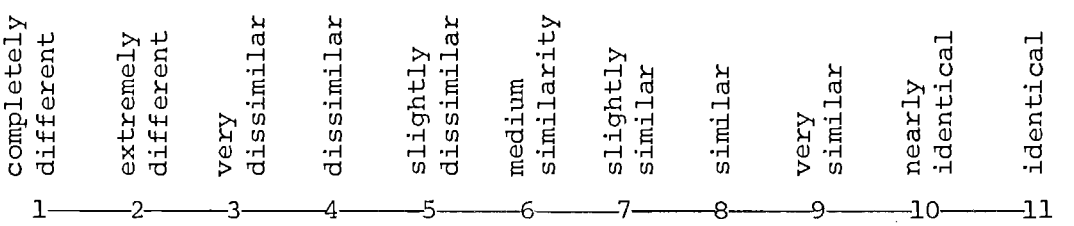
Jellinek (1959) also noted that the odorous vehicles used in perfumes have a profound effect on odour, some odorants smelling much stronger in water than in mineral oil and vice versa.

The uncertainty of the effects of solvents upon

odorants suggests that direct presentation is preferable in this case. As the odorants have a narrow molecular weight range, weighed samples of the odorants were made. A constant weight of 100 mg/flask was chosen.

Method of Response

For the pilot study pair-wise similarity assessments were selected as the judgements to be made. This type of task has been used in other studies of odour quality determination. In this situation the subject responds, for example, on the following scale:



The INDSCAL MDS program (Carroll and Chang, 1970) was selected for data analysis in this study. The INDSCAL model accounts for individual differences in similarity judgements and Carroll and Chang note that the method is limited to the case in which individual subject spaces are related by linear transformations of a common space. The INDSCAL model is a metric rather than non-metric model; presupposing scaling solutions in Euclidean space. This analysis will be discussed in greater detail later.

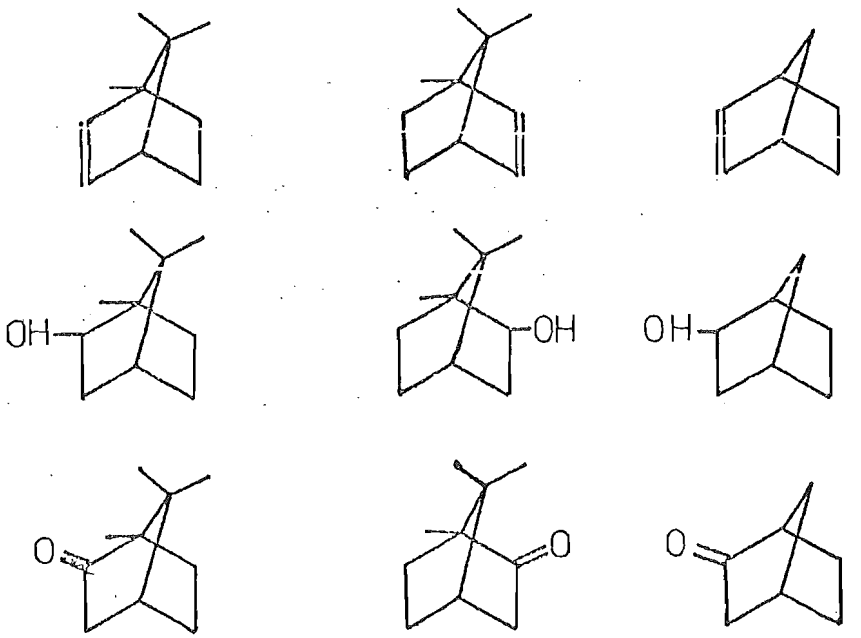
Stimuli

As outlined in previous chapters, the effect of optical activity in odour perception is of interest. In order to investigate this effect, both optical isomers of each of three bornane derivatives were prepared (see Table III-1).

In addition, three norbornane derivates were included in order to observe the effect of modifications to the molecular skeleton on perceived odour.

Table III-1

Compounds used in the Pilot Study



Sufficient quantities of each of these compounds were available to set up the entire half matrix of paired flasks (see Table III-2, p. 63).

Experimental Procedure

All 36 pairs of stimuli, in a random sequence, were laid around a well-ventilated (air conditioned) room so that subjects could move freely from one labelled position to the next, as outlined in the instructions.

Subjects were members of a Stage III level course in Psychophysics and the experiment was presented as part of their course requirements. No attempt was made to assess prior experience in experiments of this type.

The class was split into two groups (group A and group B) and these groups were run separately. Each group performed the experimental task on two separate occasions (week 1 and week 2). Group A proceeded through the stimulus series in ascending numerical order of the numbered stimulus pairs, while group B proceeded in descending numerical order. On week 2 of the study the same procedure was repeated.

All subjects were instructed to begin at different labelled positions. The initial positions were arranged to be at least three places from subjects on either side in order to allow the maximum recovery-time for the compounds between successive sniffings.

The following diagrams show the labelled bench positions, initial positions for subjects and the direction of movement by subjects during the course of the experiment.

Table III-2

Pilot Study - Group A

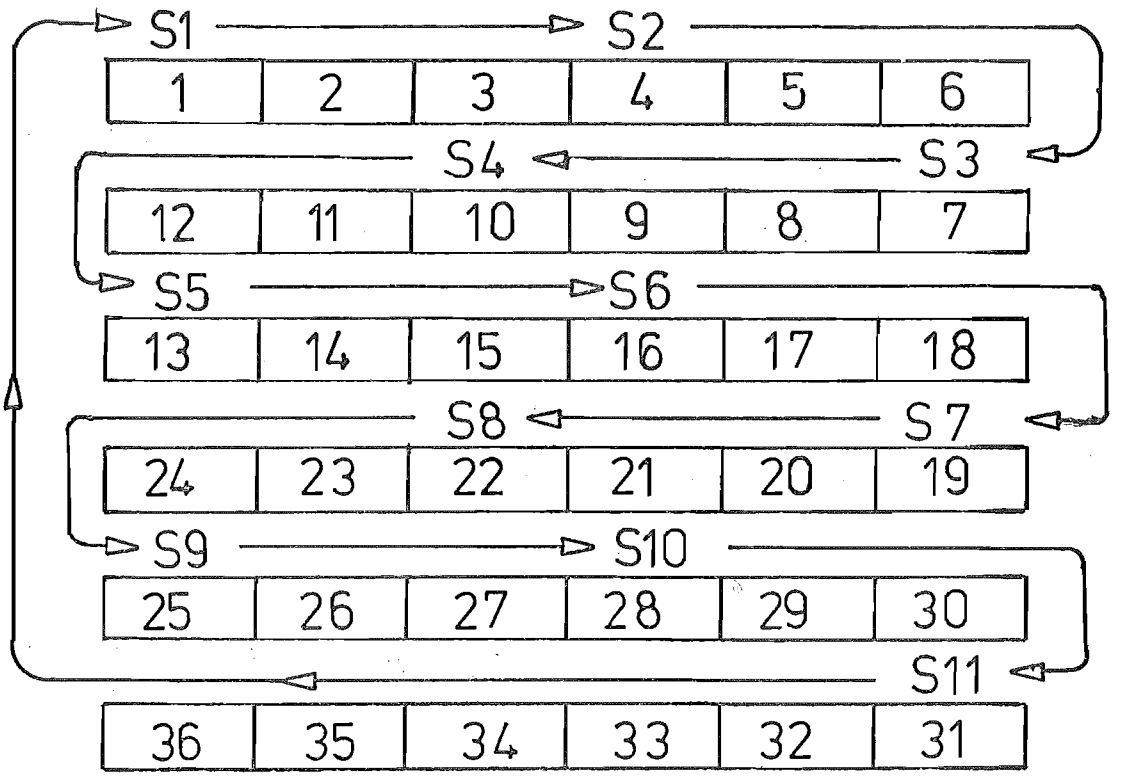
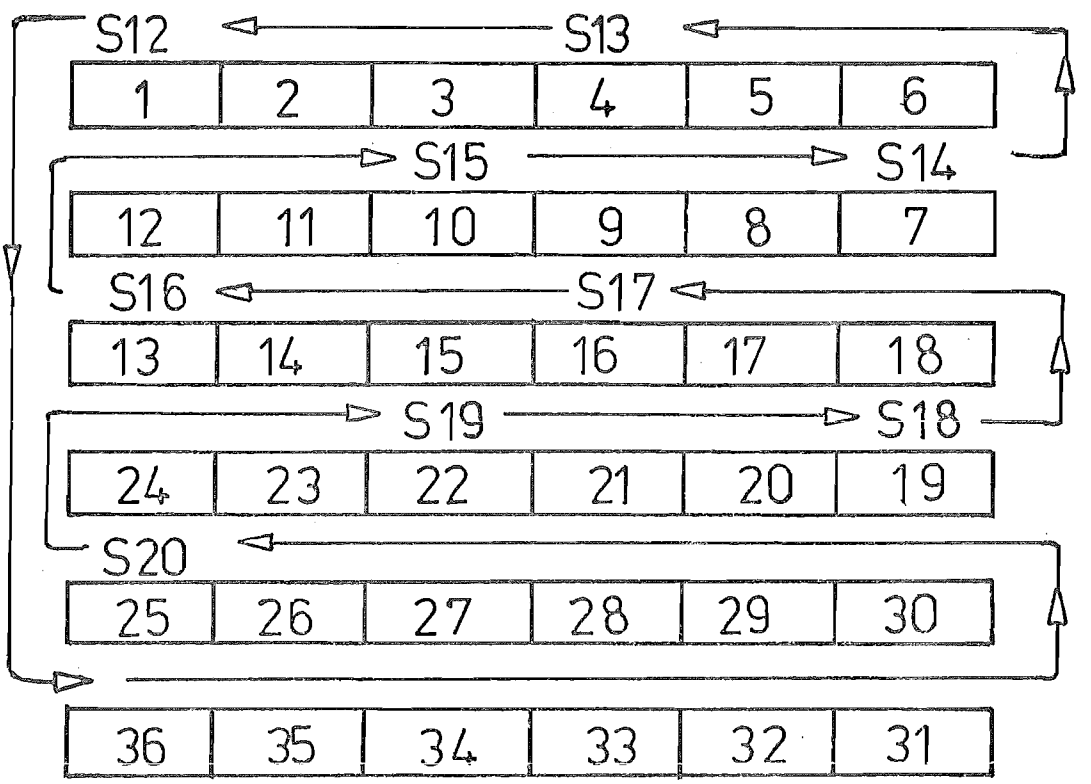


Table III-3

Pilot Study - Group B



Instructions to the subjects were read out as follows:

"(1) You have been given a scoring sheet with a box on the front (see below) which has your subject number marked in. Please note this number as you will require it next week.

SUBJECT NUMBER		BEGAN POSITION NUMBER		GROUP A or B	

"(2) The second box contains a position number and this refers to one of the 36 positions marked out on the benches. At each of these positions there are two sample bottles, labelled by the position number followed by A or B. Group A will always smell bottle A first, then bottle B. This group will always move in the direction of increasing numbers. Group B will also smell bottle A first, then bottle B. Group B will always move in the direction of decreasing numbers (see diagram).

"(3) Please note the response scale on the front of the scoring sheet. 36 such scales have been reproduced in the booklet, numbered to correspond with each bench position number. At each position you will be required to make <u>one</u> response only. This will be done by circling one of the numbers 1 to 11.

The Judgement

"When I signal "A" your task is to open the flask A and smell the contents, then close the flask. After a gap of 15 seconds I will signal "B" and you are to open flask B and smell the contents. Then record the response as follows: Your task is to say how similar the smell of the first odour is to the smell of the second odour using whatever criterion you please. Some of the odour pairs may be identical (in which case you would circle 11), some may be completely different (in which case you would circle 1), while others will be of "intermediate" similarity. Please observe the response scale once more before we begin the first trial. Note: The numbers before the response scales refer to the bench position number, not the trial number."

Results and Discussion

The scale values were divided by 100 and then used as direct input to the INDSCAL (Carroll and Chang, 1970) multidimensional scaling program. This analysis provided a set of mathematical solutions which plot the relative positions of subjects in performing the rating task (i.e. estimates of individual weights or biases in the perceptual task), as well as a set of solutions which plot stimuli positions. In all solutions the subjects 1 to 11 were group A and subjects 12 to 20 were group B. The experiment

was repeated one week later and the two sessions are referred to as "wk 1" and "wk 2".

Goodness of Fit Criteria

These measures show what proportion of the variance is accounted for by the particular n-dimensional configuration generated as a mathematical solution to the scaling problem. For example, from the table below we see that for the three dimensional solution the Average Subject Correlation Coefficient is 0.690. This would suggest that 48% of the variance is attributable to the solution. The other measure, the correlation between Y (data) and Y (hat) is 0.700, suggesting that the model accounts for 49% of the variance. The MDS program generates a set of spatial co-ordinates from other raw data; these are labelled Y (data). The program also generates a space of co-ordinates from a mathematical solution which are labelled Y (hat). The mathematical solution is achieved after a series of iterations meet the criterion of convergence.

Table III-4

Goodness of fit - Pilot Study

Av. S. Correl. Coeff.	3D	0.690
	2D	0.635
Correl. Y (data) and Y (hat)	3D	0.700
	2D	0.651

Gregson and Mitchell (1974) attribute 56% of the variance to the model (i.e. a goodness of fit of approximately 0.748).

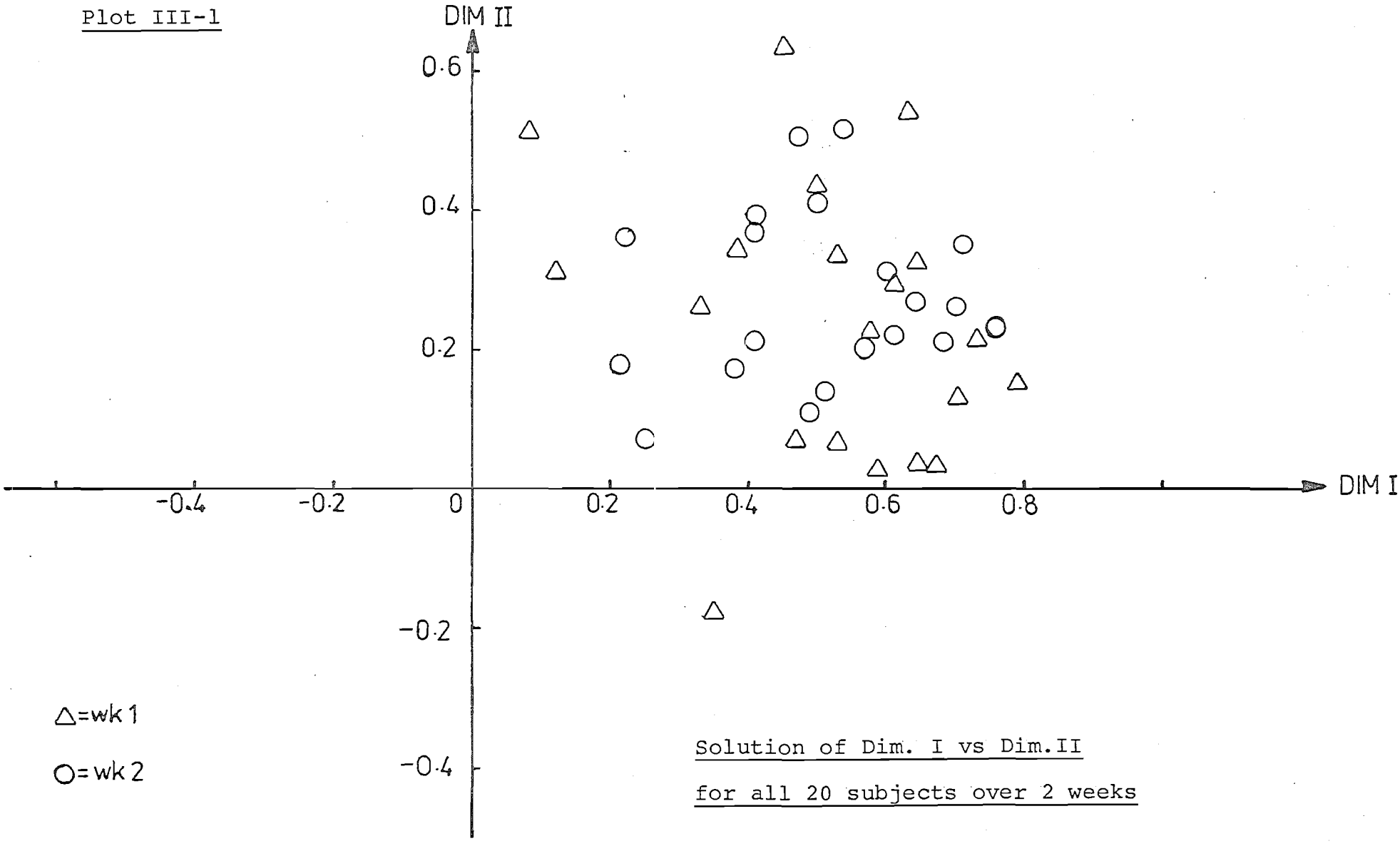
Comparison of these results with those of the Gregson study suggests that this level is adequate but the solutions leave considerable variance unexplained.

Consider firstly the "between subjects" comparisons. The plot III-1 shows Dim I vs Dim II for the 3D solution. In this plot we see firstly that all subjects are clustered together in the upper right section of the plot. This would indicate that the subjects are tending to respond homogeneously. This would justify the grouping of data for the "stimuli" plots as the subjects appear to be performing the same task in the same manner.

The plot III-1 also shows that there is no appreciable change in the distribution from week 1 to week 2. There is a slight tendency for the spread to be greater for week 1 than for week 2.

The plots III-2 and III-3 demonstrate more clearly the responses by the same subject on successive weeks. Lines are drawn to link the position of each of the twenty subjects on week 1 with the position on week 2. There is remarkable consistency in responses of individual subjects. In addition, there is no observable pattern differentiating group A from group B. From this it would be safe to assume that long-term order effects were minimal in this experiment.

Plot III-1

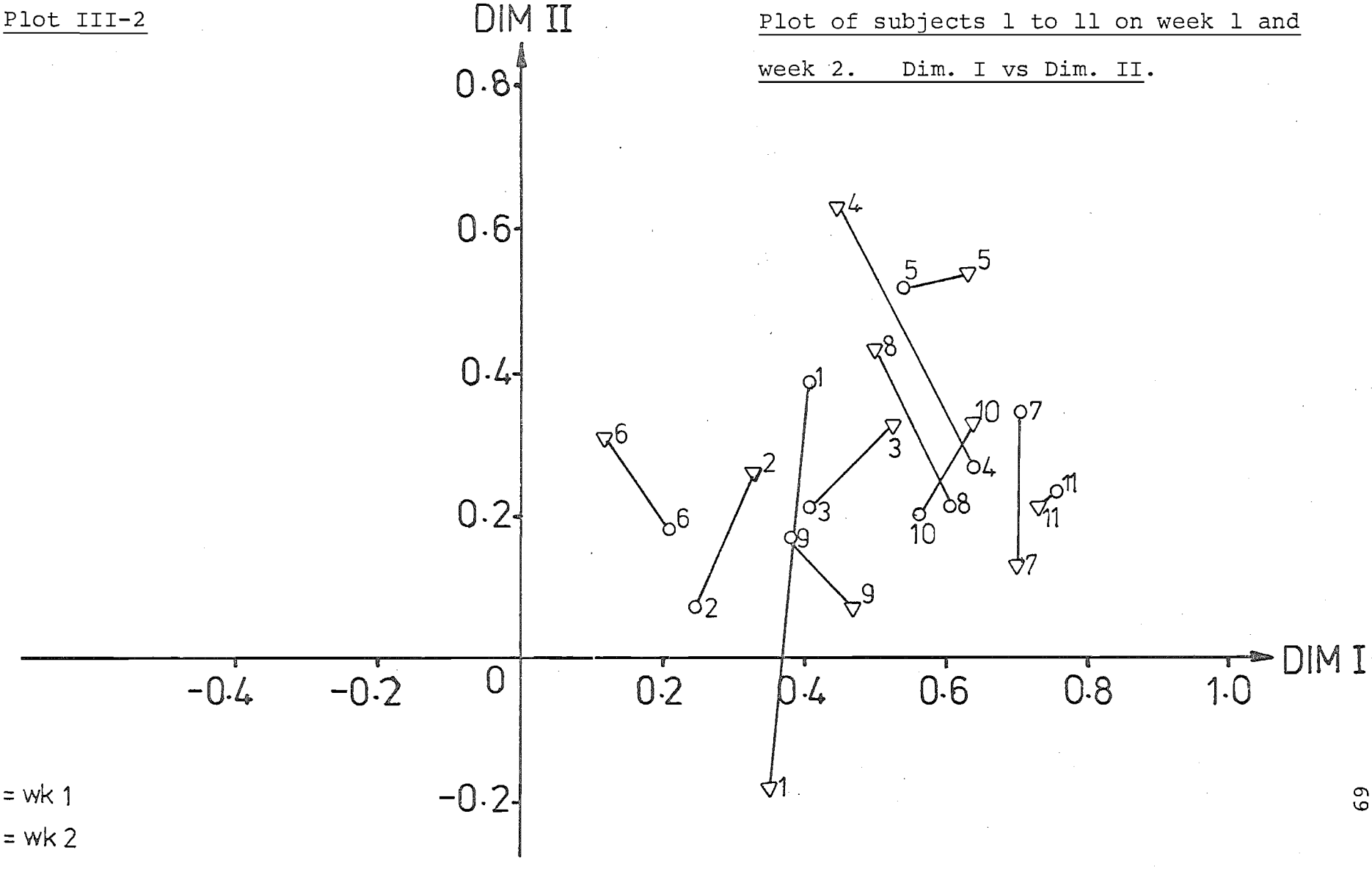


Solution of Dim. I vs Dim.II

for all 20 subjects over 2 weeks

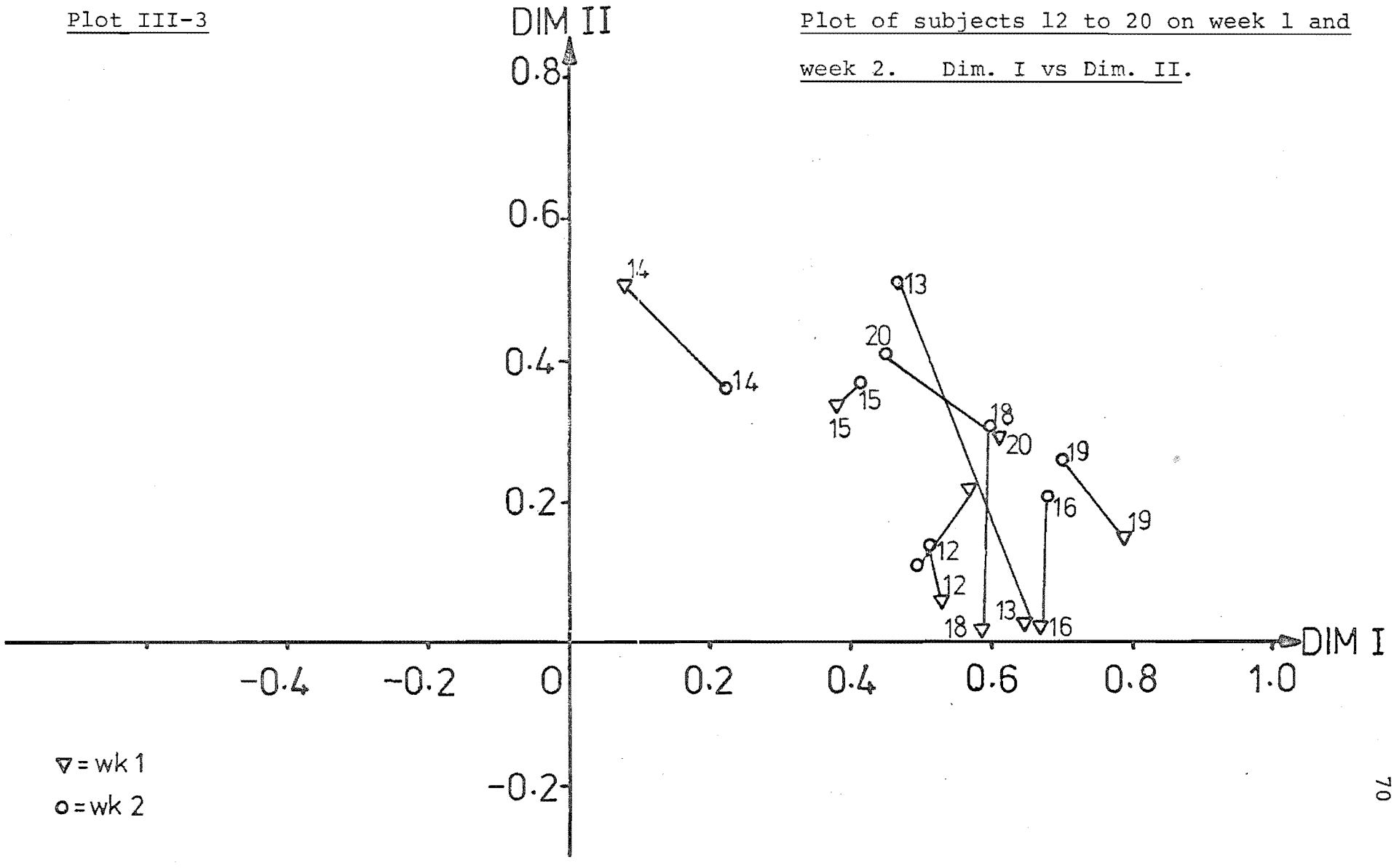
Plot III-2

Plot of subjects 1 to 11 on week 1 and week 2. Dim. I vs Dim. II.



Plot III-3

Plot of subjects 12 to 20 on week 1 and week 2. Dim. I vs Dim. II.

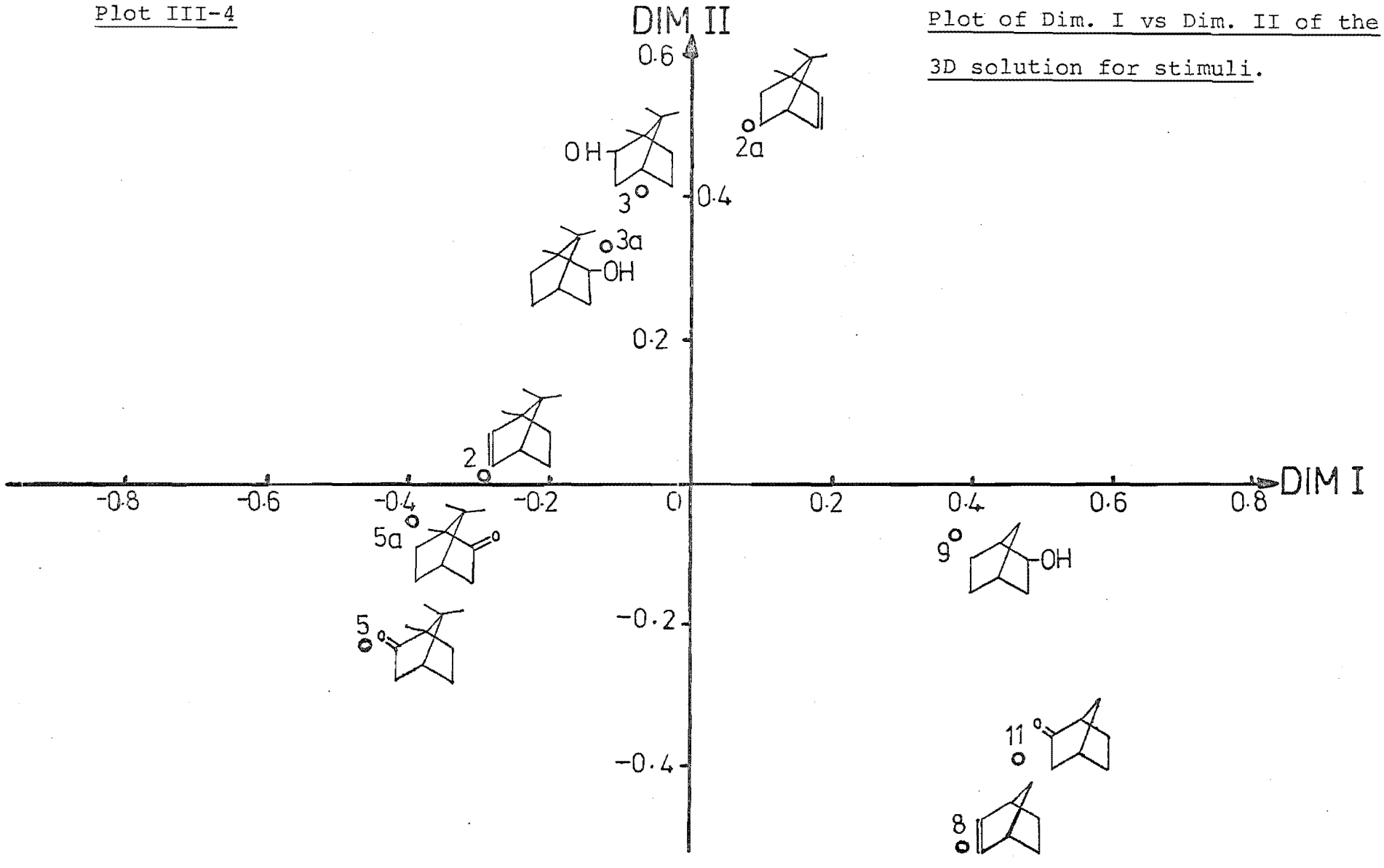


Consider now the plots for the three dimensional solution for interstimuli distances. Two plots of interstimuli distance have been included; they are plot III-4 (Dim I vs Dim II) and plot III-5 (Dim I vs Dim III).

We see from plot III-4 that the separation along Dim I forms two clusters, one of norbornane (bicyclo [2.2.1]heptane) derivatives and the other of bornane (1,7,7-trimethylbicyclo[2.2.1]heptane) derivatives. The separation along Dim II is less obvious but there is a tendency for alcohols to lie to the positive side of Dim II and the ketones and alkenes to lie on the negative side of Dim II. It appears that the compound 2(a) is an exception to this. This tendency to separate in accordance with functional group presence is more obvious on dimension III (plot III-5). The alcohols tend to lie at the positive end of Dim III and there is a tendency for the alkenes to lie at the negative end of Dim III.

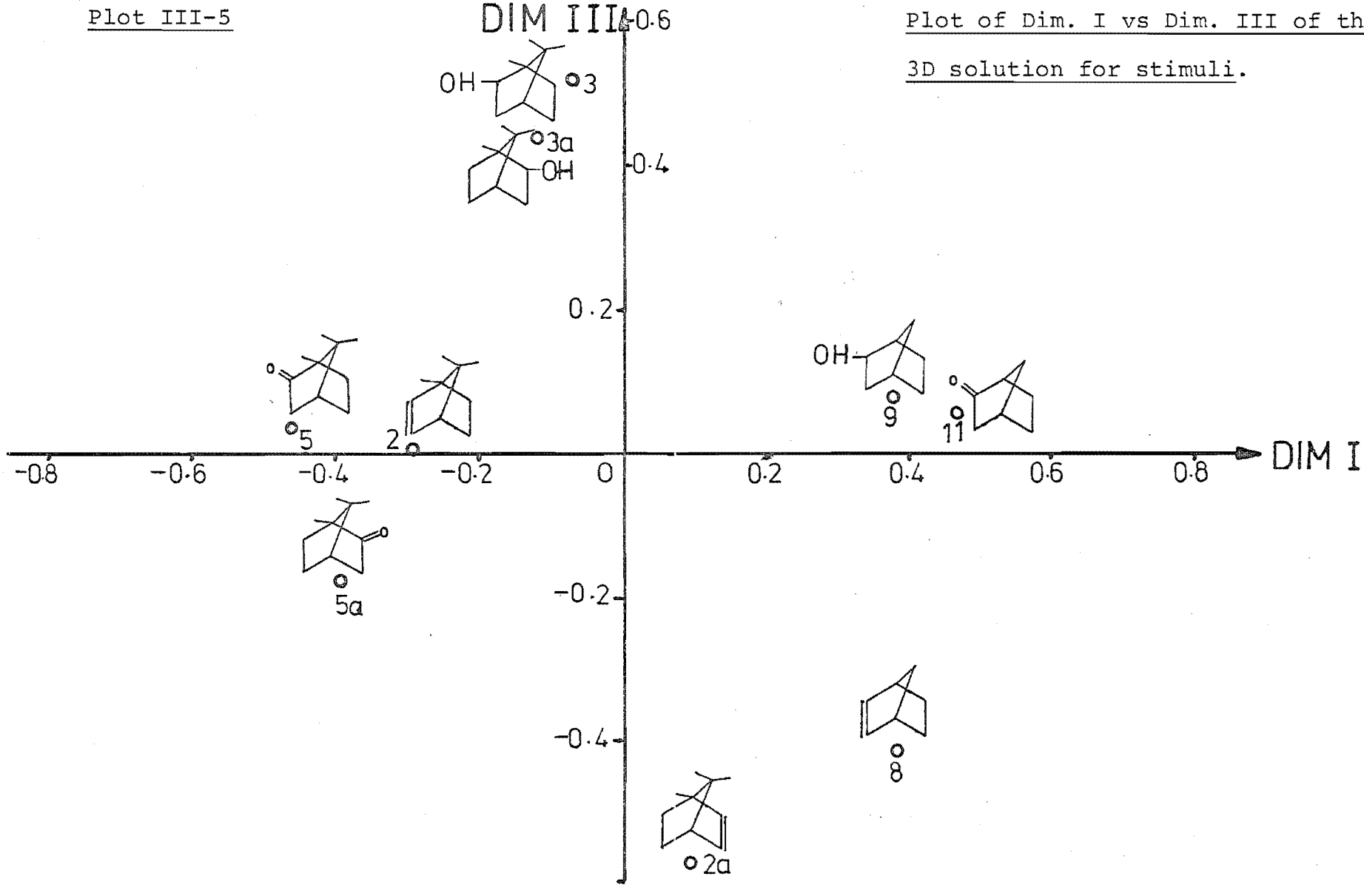
Thus a number of trends may be seen in this study. Firstly it would appear that subjects responded in a consistent manner, given the intrinsically variable nature of olfactory psychophysical data, over the two experimental sessions and that presentation order effects were minimal. There was an observable difference in the responses to bornane derivatives and norbornane derivatives. This is seen in the clustering in the plot III-4 (Dim I vs Dim II). There was, however, little variation between responses to the corresponding optical isomers (see plots III-4 and III-5). It would appear from this that further investig-

Plot III-4



Plot of Dim. I vs Dim. II of the 3D solution for stimuli.

Plot III-5



Plot of Dim. I vs Dim. III of the 3D solution for stimuli.

ation of corresponding optical isomers by this experimental technique would not be advisable. For this reason the preparation of further optically active pairs was not pursued.

There is some suggestion that Dim II and Dim III of the 3D solution show functional group separation.

Further experiments using a wider range of functional groups would be of use.

CHAPTER FOUR

VERBAL STUDY

ON THE PERCEIVED SIMILARITY OF WORD PAIRS

In order to select suitable scales for use in the major study of this thesis, it was necessary to determine verbal labels which cover the odour space most extensively. Scale labels were chosen from other studies concerned with the quality of odour (Amoore, 1970; Yoshida, 1975; Harper, Bate-Smith and Land, 1967; Woskow, 1968; and Henning, 1915 (cited in Harper et al, 1967)). There is some replication within the range used by these various workers and this allowed the list of odour words to be restricted to 20. From this base set was then constructed all possible pairs, which gives a 20 x 20 half matrix of pairs without the leading diagonal, that is, 190 paired comparison judgements in all required of each subject.

Stimulus presentation was quasi-random with the following constraints. No stimulus word was used in two successive presentations and the stimuli were alternated with respect to "position in the stimulus pair" with successive presentations.

The scale ranged from -10 (opposite) to 0 (mutually irrelevant) to +10 (synonymous). (Lundberg and Devine, 1972; Martin, 1965).

It should be noted that such a scale includes

similarity as well as the opportunity to express opposition. Opposition is thus placed at points on the axis between identity and complete dissimilarity instead of beyond the complete dissimilarity point (Martin, 1965). Lund (1974, 1975) has noted some of the difficulties involved in the use of such bipolar scales, particularly with content analyses.

The subjects were split into two groups matched for sex composition and age range. The first group, Group A, consisted of 27 subjects, 12 male and 15 female, aging from 17 to 37 years. The second group, Group B, consisted of 26 subjects, 11 male and 15 female, aging from 16 to 36 years. All subjects were selected from undergraduate Psychology classes and none had prior exposure to experiments of this type.

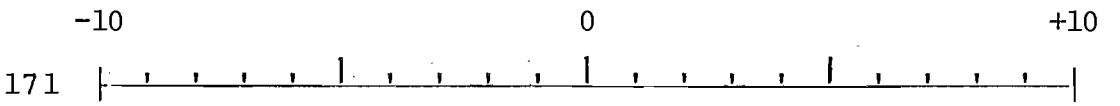
A similarity judgement task was selected for this experiment with a 10 second interval between successive presentations. These stimuli are seen in Table IV-1.

Table IV-1

Odour Words used in this study

Word	Symbol (for use in graphing)
Pleasant	PLE
Harsh	HAR
Vivid	VIV
Floral	FLO
Pungent	PUN
Camphor	CAM
Musky	MUS
Minty	MIN
Putrid	PUT
Ethereal	ETH
Sweet	SWE
Burnt	BUR
Oily	OIL
Metallic	MET
Spicy	SPI
Sulphorous	SUL
Cool	COO
Fruity	FRU
Resinous	RES
Foul	FOU

Subjects were given a response booklet which had 190 scales, numbered from 1 to 190.



Instructions to Subjects

The following instructions were read to subjects prior to the experiment:

"You will have noticed, on the front page of the booklet, a scale which has been selected for use in this experiment. It ranges from -10 (opposite) on the left to 0 (mutually irrelevant) to +10 (synonymous) on the right. This scale is repeated for each trial within the booklet.

"During the course of the experiment, words will be presented in pairs (e.g. Pleasant - Cool). Your task is to rate these on the scale given. The words are descriptive and are often used to describe odours. In this experiment consider these words as descriptions of odours.

"The pairs of stimuli will be presented for 10 seconds, so your judgement will have to be made rapidly. To make a response, circle one of the points on the scale. The scale used has a reference number situated in the left hand margin; this must match the number given with the pair of stimuli on the overhead projector.

Are there any questions before we proceed?"

Results

For analysis, the booklet scales were renumbered 0, 1, 2, ... 10, ... 18, 19, 20 for direct input to an INDSCAL MDS program (Carroll and Chang, 1970).

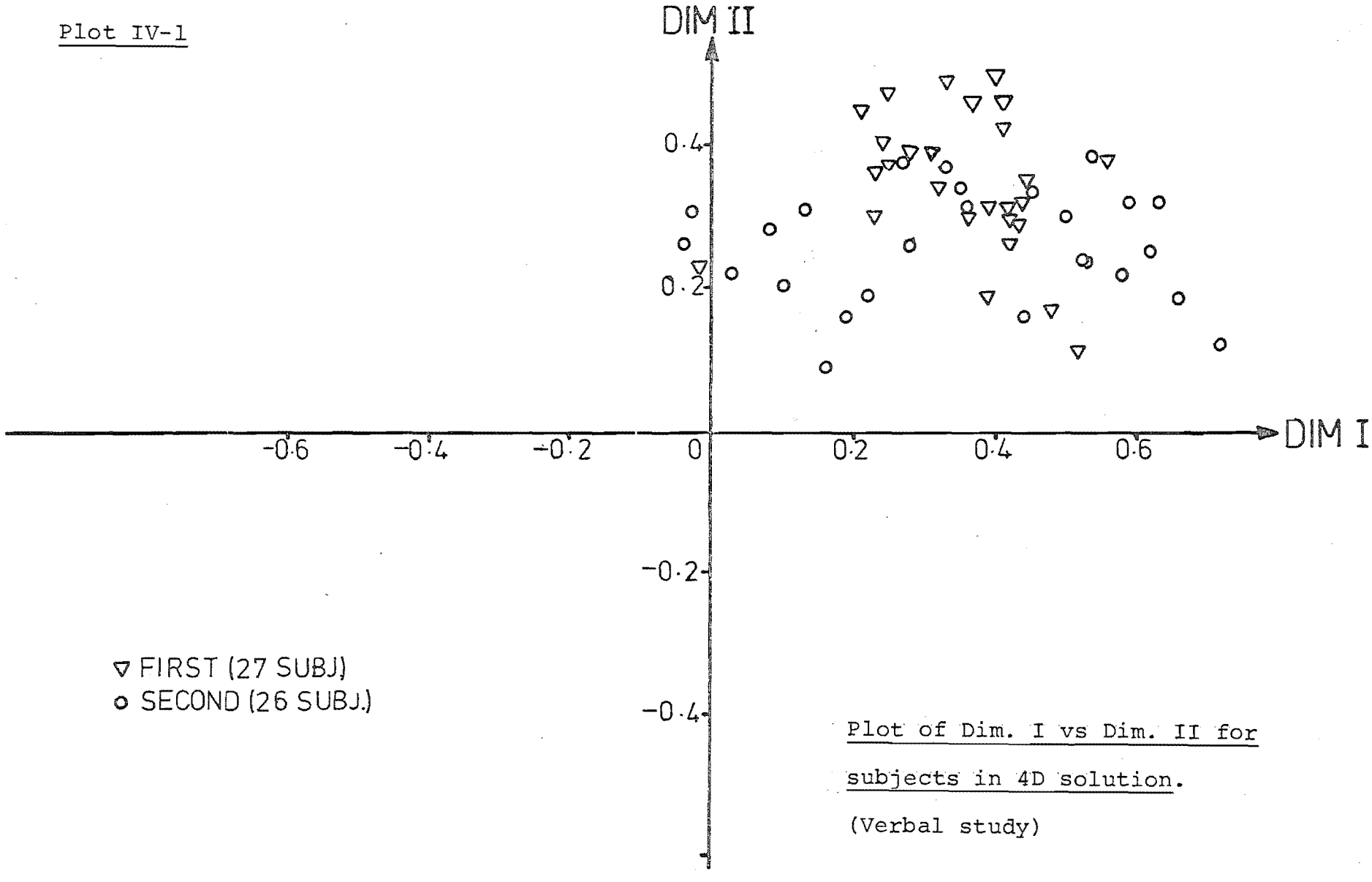
In this analysis four dimensional (4D), three dimensional (3D) and two dimensional (2D) solutions were calculated for both groups. A one dimensional (1D) solution was also performed for group A responses.

The intersubjective homogeneity in this experiment is best examined in the Dimension I vs Dimension II plot of the 4D solution (Plot IV-1). Both group A subjects and group B subjects appear to be homogeneous in responding, with group B having a slightly larger spread along Dim I than has group A. There is a slight tendency for group A to be more spread along dimension II.

These effects are slight and there is no reason to suspect that the two groups responded in a different manner. There is no evidence of clustering within groups to form subgroups with special strategies.

Consider now the plot IV-2 which plots dimension I vs Dimension II for odour word stimuli (4D solution). In this solution the odour word stimuli have been plotted for each of the two groups of subjects. Symbols are as shown in Table IV-1 for group A and the same symbol underlined for group B

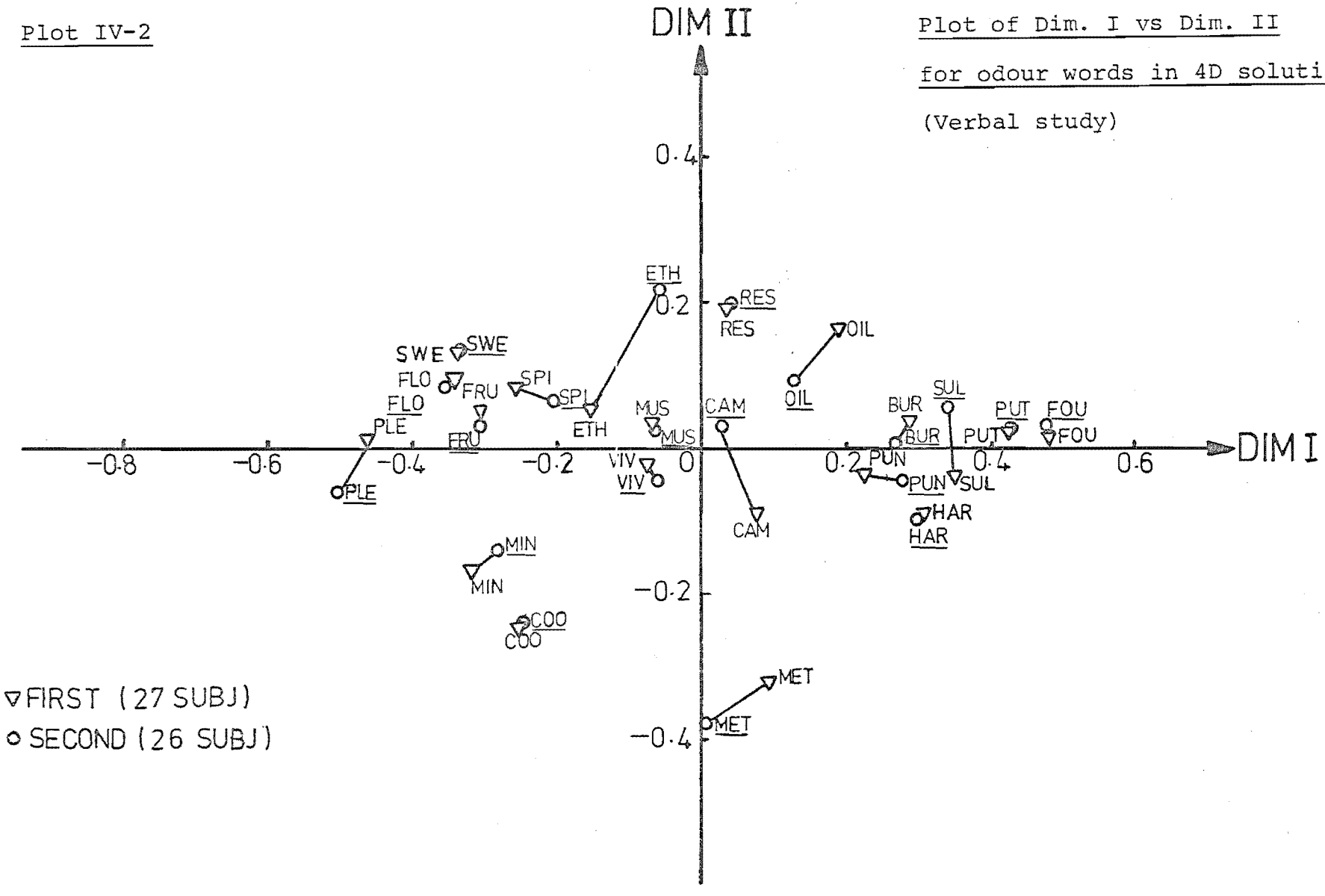
Plot IV-1



Plot of Dim. I vs Dim. II for subjects in 4D solution.

(Verbal study)

Plot IV-2



Plot of Dim. I vs Dim. II

for odour words in 4D solution.

(Verbal study)

(i.e. PLE for pleasant, group A; PLE for pleasant, group B). Lines have been drawn linking identical stimuli in the different presentations. These lines are short relative to the distances between different stimuli, indicating that between group consistency is high. Both groups have produced similar results in performing the same task.

The overall shape of the distribution is rhombic. Dimension I has putrid, sulphorous and foul at one extreme and sweet, floral and pleasant at the other. This is quite clearly a hedonic dimension. Dimension II has ethereal, resinous and oily at one extreme and minty, cool and metallic at the other. This most closely resembles a Hot-Cold dimension (see discussion).

Arabie and Boorman (1973) report a diamond-like pattern in scaling solutions where the Minkowski metric is r = 1 (city-block metric). This would be consistent with the solution pattern attained in the current study and may suggest that the subjects were responding as above.

Consider now the goodness of fit criteria. The Table IV-2 below shows the average subject correlation coefficients for the 1D to 4D solutions as well as the correlation between Y (data) and Y (hat) (discussed in Chapter III).

Table IV-2

Goodness of fit criteria

Average Subject Correlation Coefficient

	Group A	Group B
4D	0.6898	0.6033
3D	0.6778	0.5759
2D	0.6528	0.5399
1D	0.6163	Not Calculated

Correlation between Y (data) and Y (hat)

	Group A	Group B
4D	0.6982	0.6230
3D	0.6864	0.6023
2D	0.6612	0.5721
1D	0.6294	Not Calculated

In selecting appropriate solutions for discussion it is necessary to consider goodness of fit. Gregson and Mitchell (1974) took a case of 56% variance accounted for as a tenable representation, ruling out solutions of lower dimensionality as being trivial. In this study the added variance with added dimensionality is small so that the 2D solution is the most acceptable. In all cases Dimension I accounts for a large proportion of the variability in the system. This dominance of the hedonic dimension is not unusual in olfaction. Dimensions I and II will be accepted in description of these results.

Discussion

Individual subjects appear to be responding in a consistent manner in each of the two groups. There is no apparent difference in the response patterns of the two groups of subjects.

The 2D solution is adequate to describe the response pattern for stimuli. There was no difference between groups in their responses to stimuli. The results are consistent with those mentioned previously in that the major dimension appears to be hedonic. The second dimension appears to be Hot-Cold. This is in agreement with Yoshida (1972) who obtained a solution in which floral, musky, minty and camphoraceous were found on the negative side of Dim I and ethereal, putrid and pungent were on the positive side. Yoshida labelled

the Dimension II as (Cool-Harsh) vs (Warm-Soft) which corresponds to that found here.

The 3D and 4D solutions have not been included as they account for such a small amount of the variance. However, there is some suggestion that Dim III may relate to "vividness" of the odour word stimuli and Dim IV appears to relate to an "Inorganic-Organic" component.

The selection of appropriate stimulus words for the response scales in the major study is made from these results. From the rhombic distribution of the 4D solution (Dim I vs Dim II) stimulus words were selected which were furthest apart, to give the best possible coverage of the verbal odour space.

The 9 stimuli were chosen as shown:

PLEASANT

MINTY

METALLIC

HARSH

FOUL

OILY

RESINOUS

SWEET

CAMPHOR

Summary

The verbal study was carried out in order to select odour words for the major study. It was necessary that the odour words span the odour word space and that odour words should have comparable meaning for all subjects. In addition the odour word space should demonstrate an interpretation comparable to that found by other authors.

All these objectives are met.

CHAPTER FIVE

MAJOR STUDY

This study will be reviewed in two chapters. Chapter V covers the overall outline of the experimental design and then considers each of the four experimental groups (see Table V-1 below) within the design, with regard to procedure, data conversion, analysis and results. Chapter VI discusses the results, both in relation to other groups within this study and in relation to other studies of this type.

Table V-1

Experimental Design for the Major Study

Group Number	I (15 Subjects)	II (15 Subjects)	III (15 Subjects)	IV (15 Subjects)
Presentation Order of Odour Stimuli	5 Anchor 18 Struct 5 Anchor 18 Struct	18 Struct 5 Anchor 18 Struct	18 Struct 18 Struct	5 Anchor 5 Anchor

Experimental Design

The stimuli for this study are structurally related compounds of three core molecule types and some anchor compounds which are reference odours commonly used in research of this type.

Consider firstly the structurally related compounds. Correct chemical names for these compounds have been given in Chapter II of this thesis; common names have also been given. Unless specifically noted the common names will be used here.

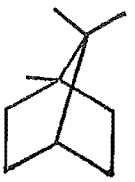
The first group consists of six bornane derivatives as follows: bornane, (1R,4R)-born-2-ene, (1R,4R)-camphor, (1R,2R,4R)-bornan-2-ol, (1R,2R,4R)-born-2-yl acetate and (1R,2S,3R,4S)-2,3-epoxybornane (See Table V-2).

The second group of six compounds are norbornane derivatives. These are as follows: norbornane, norborn-2-ene, norcamphor, exo-norbornan-2-ol, exo-norborn-2-yl acetate and 2,3-exo-epoxynorbornane (See Table V-2).

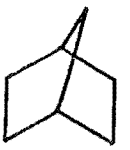
The third group consists of six cyclohexane derivatives as follows: cyclohexane, cyclohexene, cyclohexanone, cyclohexanol, cyclohexyl acetate and epoxycyclohexane (See Table V-2).

These three groups of six compounds form the basic collection of structurally related compounds for this study. These are referred to as "18 Struct" in Table V-1.

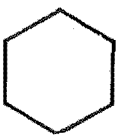
Table V-2



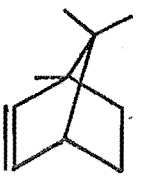
bornane



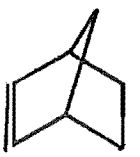
norbornane



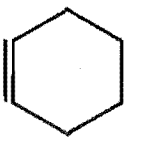
cyclohexane



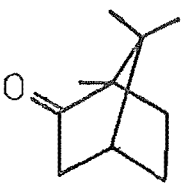
(1R,4R)-born-2-ene



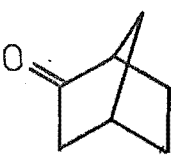
norborn-2-ene



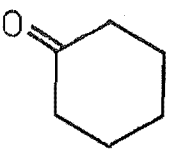
cyclohexene



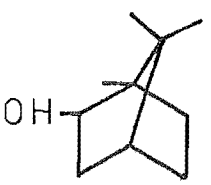
(1R,4R)-camphor



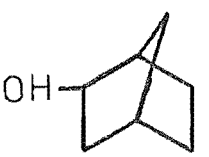
norcamphor



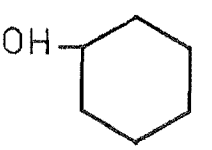
cyclohexanone



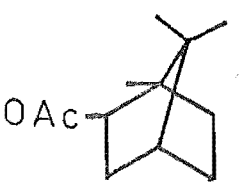
(1R,2R,4R)-
bornan-2-ol



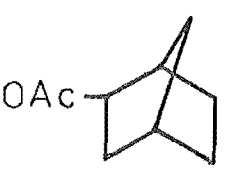
exo-norbornan-2-ol



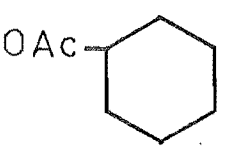
cyclohexanol



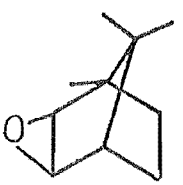
(1R,2R,4R)-born-2-yl
acetate



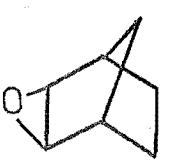
exo-norborn-2-yl
acetate



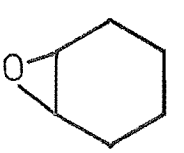
cyclohexyl
acetate



(1R,2S,3R,4S)-
2,3-epoxybornane



2,3-exo-epoxynorbornane

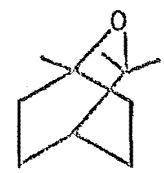


epoxycyclohexane

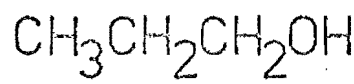
Table V-3

Anchor compounds used in this study

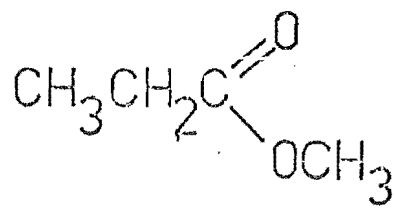
1,8-cineole



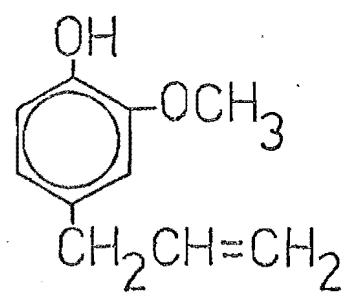
n-propanol



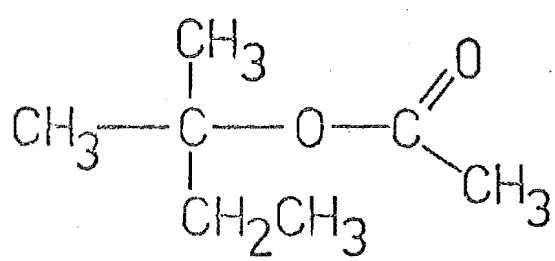
methylpropionate



eugenol



isoamylacetate



In addition to the structurally related compounds, a selection of reference compounds ("Anchor" compounds) was also included in this study. These reference compounds were as follows: isoamylacetate, n-propanol, 1,8 cineole, eugenol and methyl propionate. These compounds have been used in other studies of this type (Gregson and Mitchell, 1974; Amoore, 1970) and are treated separately from the structurally related compounds (See Table V-3).

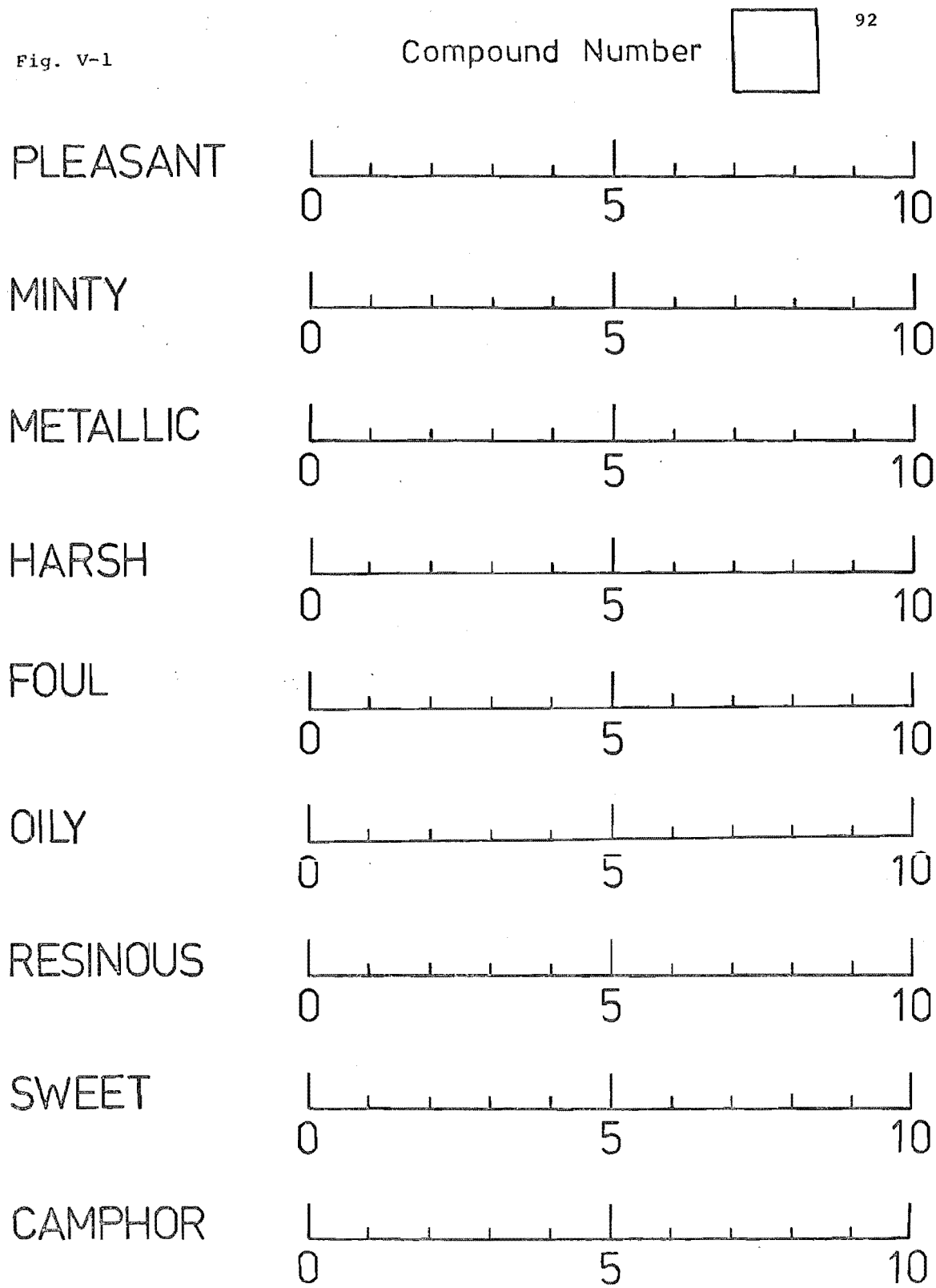
Two randomised orders were determined for each of the groups discussed this far ("18 Structural" and "5 Anchor"). The presentation order for the four subject groups (Group I, Group II, Group III and Group IV) was as shown in Table V-1.

In all cases where a series of compounds was used on more than one occasion for a particular subject group, a second randomised order was used for the second presentation. The same randomised sequence was used for all first presentations and the second randomised sequence was used for all second presentations.

The rating scales used for this experiment were semantic scales labelled with odour words selected previously (Chapter IV). There were nine scales in all: Pleasant, Minty, Metallic, Harsh, Foul, Oily, Resinous, Sweet and Camphor (See Fig. V-1).

Each subject was to rate all stimuli on each of the nine rating scales. A booklet with the appropriate number of pages was provided and subjects filled in the

Fig. V-1


Compound Number
PLEASANT
0
5
10
MINTY
0
5
10
METALLIC
0
5
10
HARSH
0
5
10
FOUL
0
5
10
OILY
0
5
10
RESINOUS
0
5
10
SWEET
0
5
10
CAMPHOR
0
5
10

box at the top right hand corner with the coded number given for each flask containing odorous material.

Fifteen subjects were assigned to each of four experimental groups (Group I, Group II, Group III and Group IV) and these groups were matched for sex and age content as far as was possible.

Fifty of the subjects were Stage I psychology students, most of whom had previously participated in the verbal study. The remaining ten subjects were recruited from other sources. None of the subjects reported having had any prior exposure to experiments of this type.

Stoppered 25 ml sample bottles were used for stimulus presentation. These flasks were numbered for subject identification with the numbers 1 to 46 inclusive. 100 mg of substance was placed in each bottle.

The subject was seated in the olfactometer in the Chemical Senses laboratory of the Psychology Department (See Fig. V-2) with a rising, forced stream of fresh filtered and temperature, humidity conditioned air passing through continuously. A one minute cycle began when a buzzer was sounded and a numbered flask was presented through a small hatch. The subject then opened the flask, inhaled and began responding. Upon completion of the response requirements the subject stoppered the flask and returned it to the hatch. The subject was then able to breathe fresh air until the next cycle began.

Fig. V-2

Instructions to subjects:

"Could you please fill out the details on the front of the booklet. It is necessary to fill in Name, Age and Sex.

Experimental Task

"You will have noticed, on the front page of the booklet, a scale which has been selected for use in this experiment. It ranges from 0 (Not at all) to 10 (Extremely). If you now turn to the first page you will observe that this scale has been presented 9 times for 9 different odour qualities.

"During the course of the experiment you will be presented with small flasks which contain a numbered substance. Your task is briefly to smell the substance and then rate it on each of the 9 scales.

"Could you first enter the number of the flask in the box provided at the top of the page.

"Now, consider the odour in relation to its pleasantness. If you consider it to be not at all pleasant then circle the bar above 0 on the "Pleasant" Scale. If you consider the odour to be extremely pleasant then circle the bar above 10 on the scale. If you consider the odour to be of some intermediate pleasantness you may circle any of the bars between 0 and 10, remembering that the degree of pleasantness increases as you move to the right. You have to repeat the process for each of

the other 8 scales.

"The next substance will be presented to you after an interval of one minute. You are to repeat the entire process with each of the numbered substances.

"Remember, you have one minute to rank each substance on each of 9 scales so do not spend too much time on each judgement.

"Have you any questions?"

Results

The results for each of the four groups are now presented including the data conversion and analysis. Each of the groups will be considered separately.

Group I

In all experimental sessions subjects were tested individually. Subjects (9 male, 6 female) were seated in the chamber of the olfactometer and issued with a set of instructions and a response booklet. When a subject had completed the requirements for indicating age and sex on the response booklet and indicated readiness to begin, a buzzer was sounded and flask 1 was presented. After a period of one minute the flask was removed, a buzzer was sounded and a new flask was presented. This procedure was continued until all 46 flasks had been presented. The presentation order was 1, 2, 3, ... 45, 46.

The scores from the rating scales were taken

directly (i.e. 0 to 10 inclusive). These were then averaged over the 15 subjects for each of the stimuli on each response scale. (The successive presentations of one stimulus were treated separately.) Euclidean distances were generated from these averages, resulting in a half matrix of raw data synthetic distances which was then used as input for multidimensional scaling.

POLYCON (Young, 1973) was the MDS program used for this analysis because that program is able to take the raw data distance matrix as direct input. (INDSCAL, the MDS program previously used does not have this input capability in the version locally available.)

5, 4 and 3 dimensional solutions were generated and in all cases linear fit (disparities on the x-axis, distance on the y-axis) was good. Stress was low for all solutions (See Table V-4).

Table V-4

Table of stress values for all SOLNs of MAJOR STUDY

	Group I	Group II	Group III	Group IV
5 D	0.055	0.058	0.048	Not Calculated (degenerate on 10 stimuli)
4 D	0.081	0.078	0.067	0.071
3 D	0.105	0.121	0.120	0.160
	(46 Stimuli)	(41 Stimuli)	(36 Stimuli)	(10 Stimuli)

Plot V-1

Frequency distribution plot for interdistance measures for Group I.

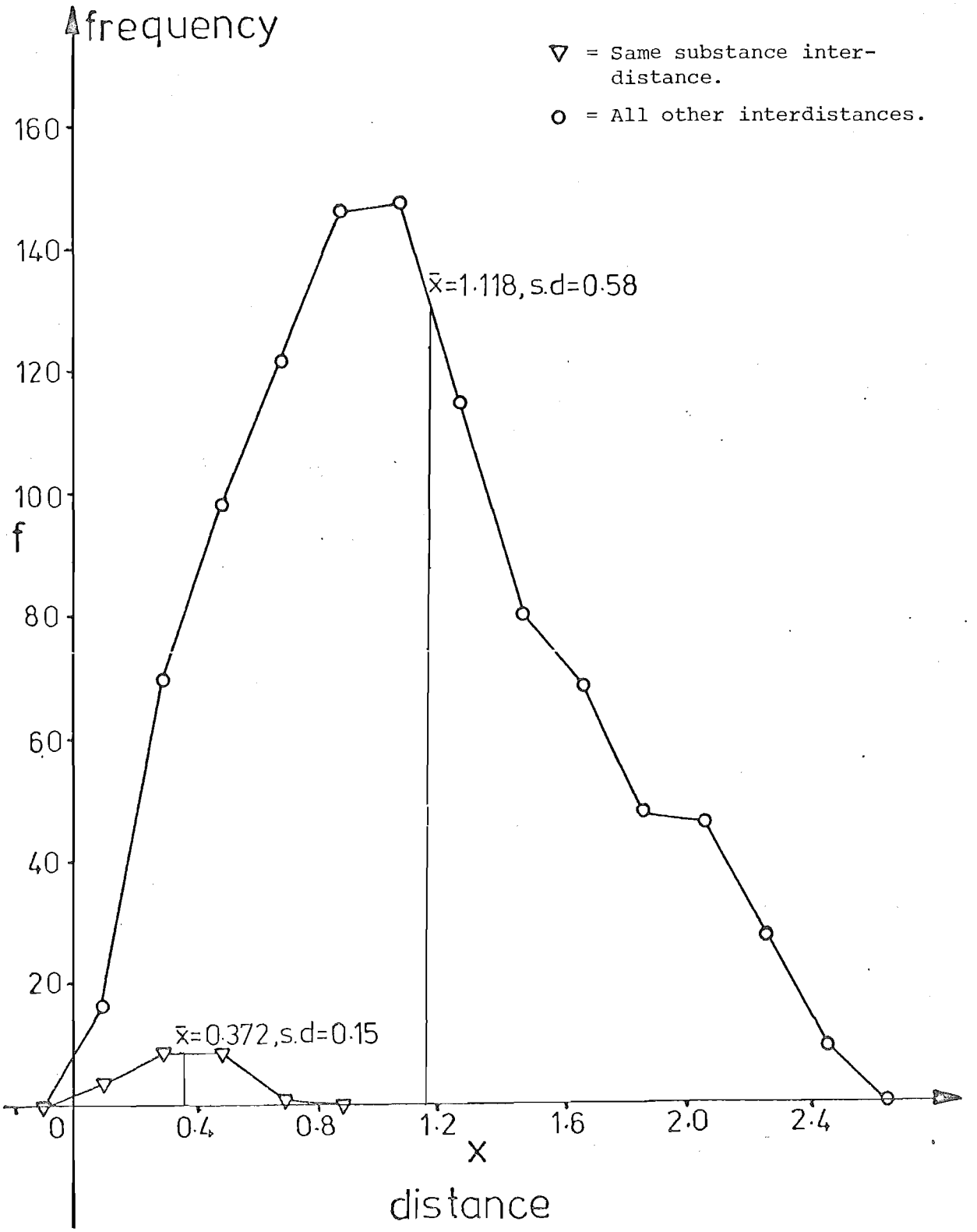


Table V-5

NOMENCLATURE FOR USE IN GRAPHING. MAJOR STUDY.

	GROUP I		GROUP II		GROUP III		GROUP IV	
	Pre 1	Pre 2	Pre 1	Pre 2	Pre 1	Pre 2	Pre 1	Pre 2
Isoamylacetate	A1	A2		A4			A7	A8
Methylpropionate	B1	B2		B4			B7	B8
n-Propanol	C1	C2		C4			C7	C8
Eugenol	D1	D2		D4			D7	D8
1,6 Cineole	E1	E2		E4			E7	E8
(1R,2R,4R)-Born-2-yl acetate	F1	F2	F3	F4	F5	F6		
Norcamphor	G1	G2	G3	G4	G5	G6		
Cyclohexanol	H1	H2	H3	H4	H5	H6		
Cyclohexene	I1	I2	I3	I4	I5	I6		
(1R,4R)-Born-2-ene	J1	J2	J3	J4	J5	J6		
2,3exoEpoxynorbornane	K1	K2	K3	K4	K5	K6		
Epoxycyclohexane	L1	L2	L3	L4	L5	L6		
Bornane	M1	M2	M3	M4	M5	M6		
(1R,2S,3R,4S)-2,3-Epoxybornane	N1	N2	N3	N4	N5	N6		
exo-Norborn-2-yl acetate	O1	O2	O3	O4	O5	O6		
Norbornane	P1	P2	P3	P4	P5	P6		
Cyclohexane	Q1	Q2	Q3	Q4	Q5	Q6		
(1R,4R)-Camphor	R1	R2	R3	R4	R5	R6		
(1R,2R,4R)-Bornan-2-ol	S1	S2	S3	S4	S5	S6		
Cyclohexylacetate	T1	T2	T3	T4	T5	T6		
Norborn-2-ene	U1	U2	U3	U4	U5	U6		
exo-Norbornan-2-ol	V1	V2	V3	V4	V5	V6		
Cyclohexanone	W1	W2	W3	W4	W5	W6		

Consider firstly the plot for Group I of Dim I versus Dim II for the 3D solution (Fig. V-3).

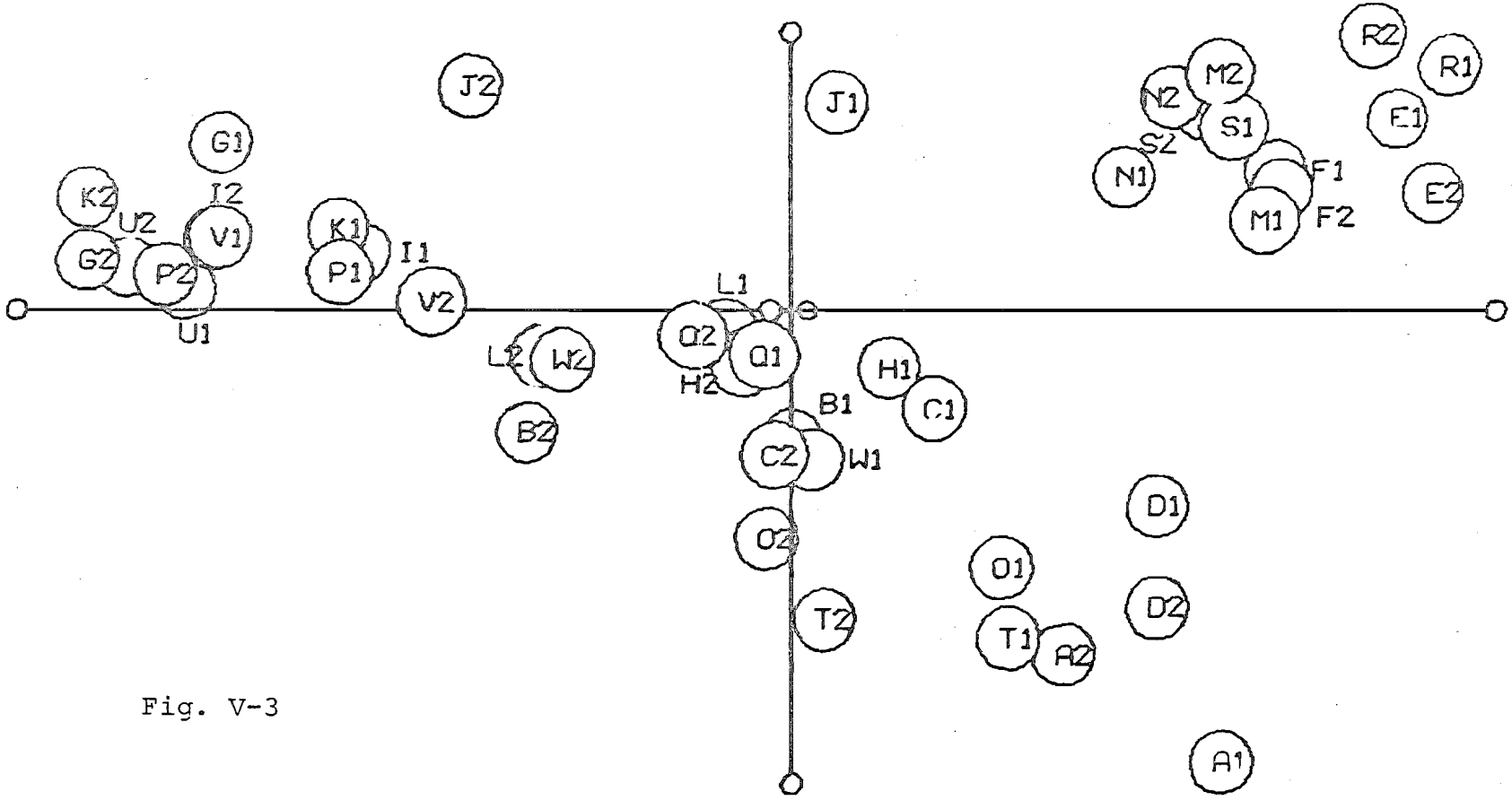

J2
J1
R2
R1
M2
N2
S1
E1
S2
F1
N1
E2
M1
F2
G1
I2
K2
U2
V1
K1
I1
G2
P2
P1
V2
U1
L1
L2
W2
Q2
Q1
H1
H2
B1
C1
B2
C2
W1
D1
O2
O1
D2
T2
T1
A2
A1

Fig. V-3

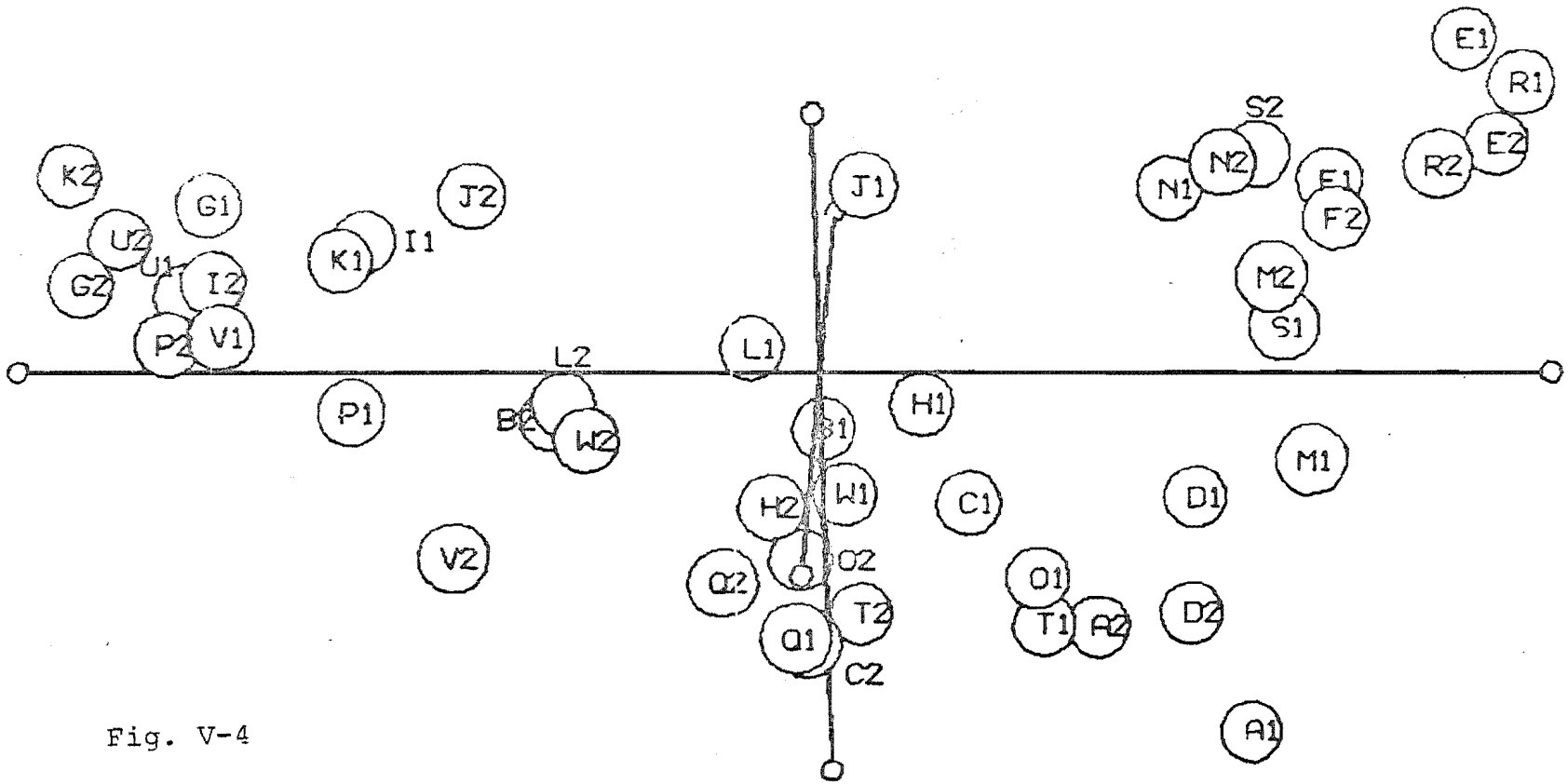

E1
R1
S2
N2
E2
R2
K2
G1
J2
J1
N1
E1
F2
U2
K1
I1
U1
I2
M2
G2
S1
P2
V1
L2
L1
P1
H1
M1
W1
H2
C1
D1
O2
V2
O1
T2
T1
D2
C2
A1

Fig. V-4

A three dimensional view of the entire solution is presented at the rear of this thesis (Appendix 2). The stereo views were generated by computer using the ORTEP II program (Johnston, 1970) and these may be viewed with the aid of a small stereoscope. In addition to the solution mentioned above, a second solution is included where the z axis has been rotated 30^{o} into the page. This also is included as a 2D plot (Fig. V-4) and a 3D plot (appendix 2). The 30^{o} rotated plot is included to show more clearly any of the stimuli obscured in the original plot and to give a second view of the clusters of stimuli. Discussion of this clustering is offered in Chapter VI.

Group II

Once again all the subjects were tested individually in all experimental sessions. Subjects (7 male, 8 female) were seated as for Group I and were issued with a set of instructions and a response booklet. When a subject had completed the requirements for indicating age and sex on the response booklet the experimental sequence was begun as for Group I. Flasks were presented in the following order: 6, 7, 8, ... 22, 23, 24, ... 45, 46.

Scores were taken from the rating scales and treated as for Group I to generate Euclidean distances for input to the MDS. POLYCON was the MDS program used for this analysis.

Linear fit was good and stress was low for this

solution (See Table V-4). A frequency plot was drawn which plotted the distance measures between like stimuli against frequency. A separate plot was made of the interdistance between unlike stimuli versus frequency and means and standard deviations were calculated (See Plot V-2). Again the overall shape of the interdistance distribution plot is of the Chi-square type, indicating that the metric assumptions for the MDS are justified.

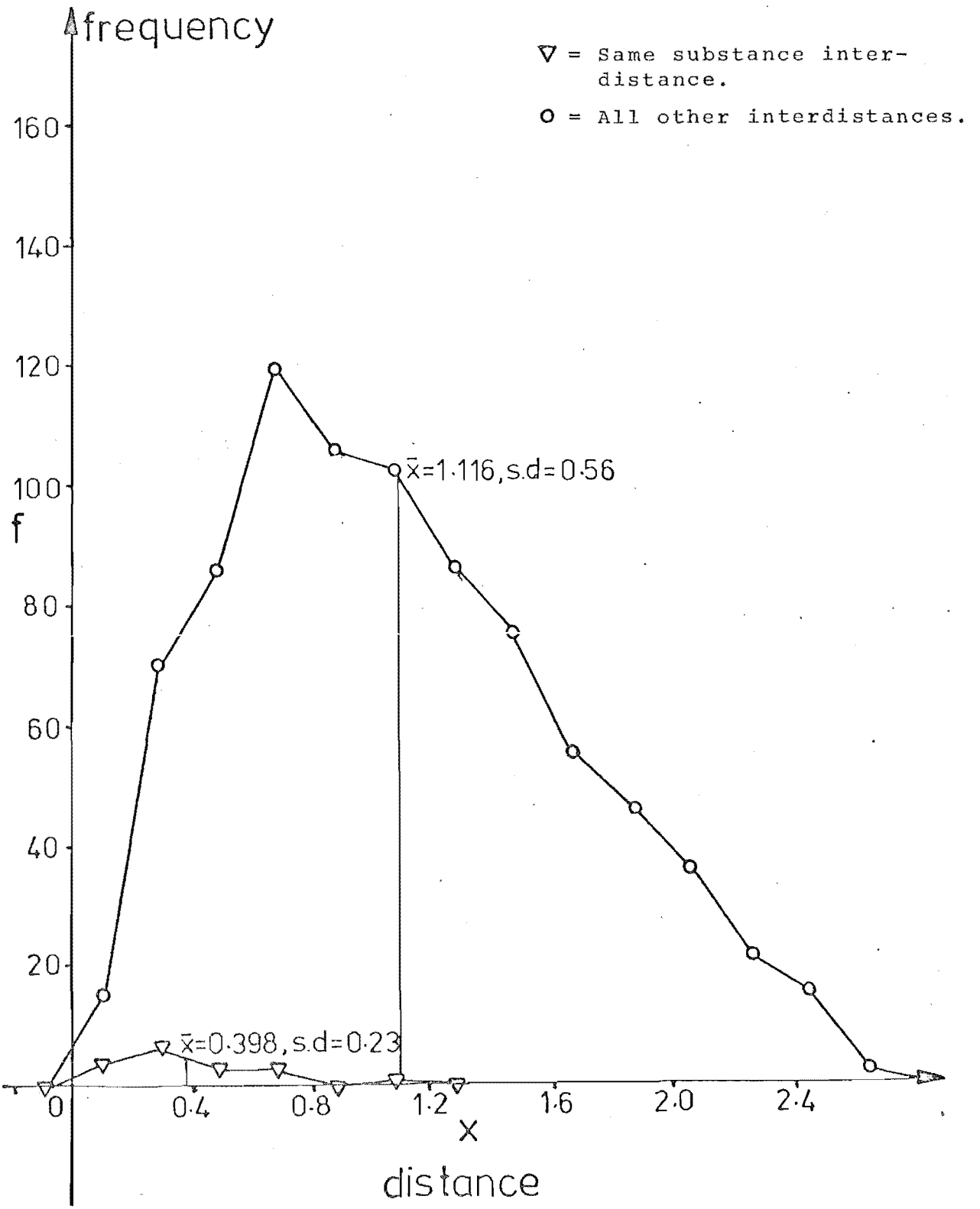
Stimuli are labelled as before, stimuli 6 to 23 are labelled F3, G3, H3, ... V3, W3 and stimuli 24 to 46 are labelled A4, B4, C4, ... V4, W4 (See Table V-5).

Consider firstly the plot of Dim I vs Dim II for the 3D solution (Fig. V-5).

A three dimensional view of this plot is seen in Appendix 2 of this thesis. Also included is a second solution where the z axis has been rotated 30^{o} into the page. As before this is included as a 2D plot (Fig. V-6) and a 3D plot (Appendix 2). The 30^{o} rotated plot is included to show more clearly any of the stimuli obscured in the original plot and to give a second view of the clusters of stimuli. Discussion of this clustering is offered in Chapter VI.

Plot V-2

Frequency distribution plot for inter-distance measures for Group II.



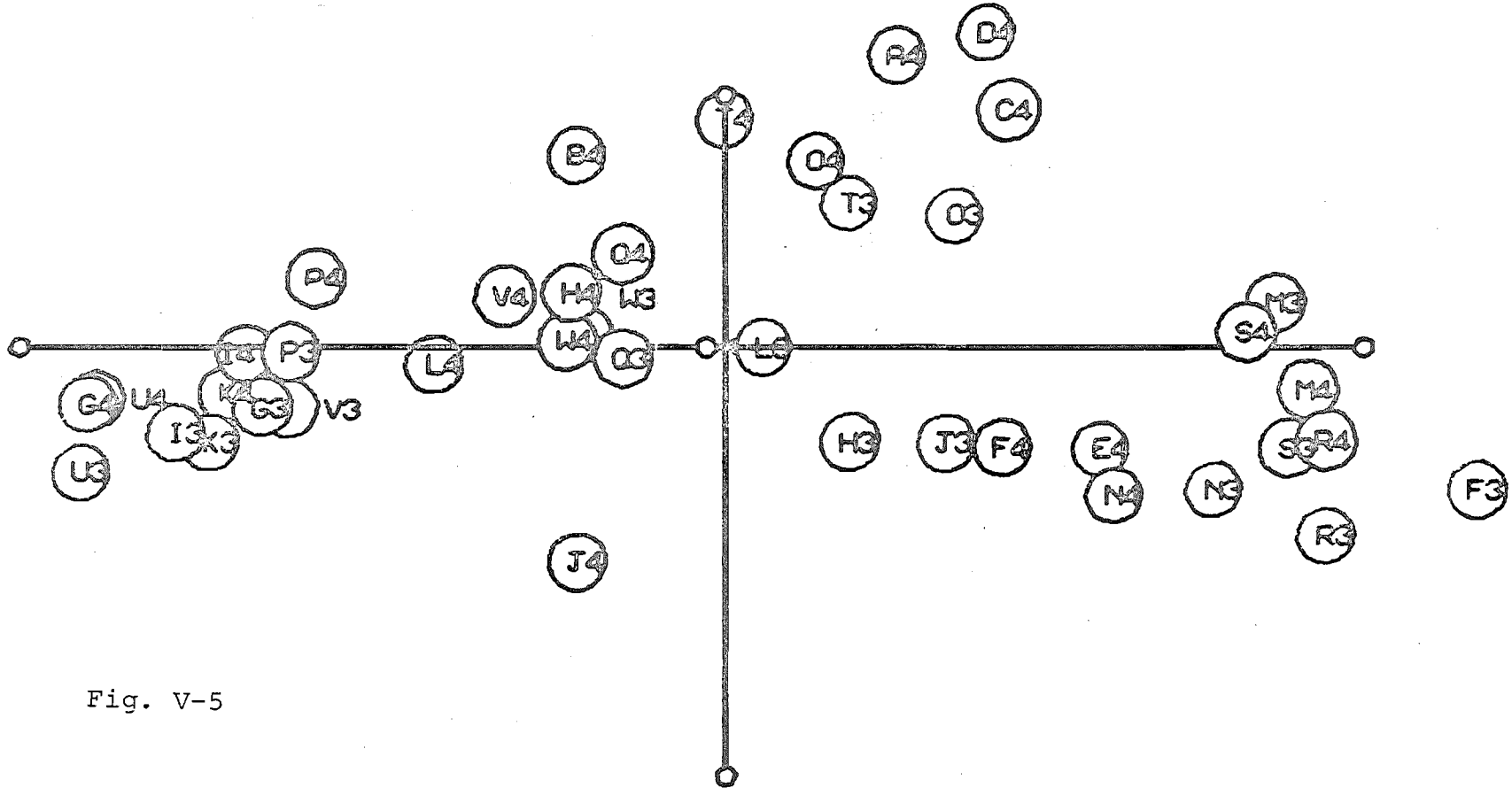

R4
D4
C4
T4
B4
O4
T3
O3
Q4
P4
V4
H4
L3
W4
O3
P3
T4
L4
L3
S4
M3
K4
G3
V3
M4
I3
X3
H3
J3
F4
E4
S3
R4
U3
N4
N3
F3
R3
J4

Fig. V-5

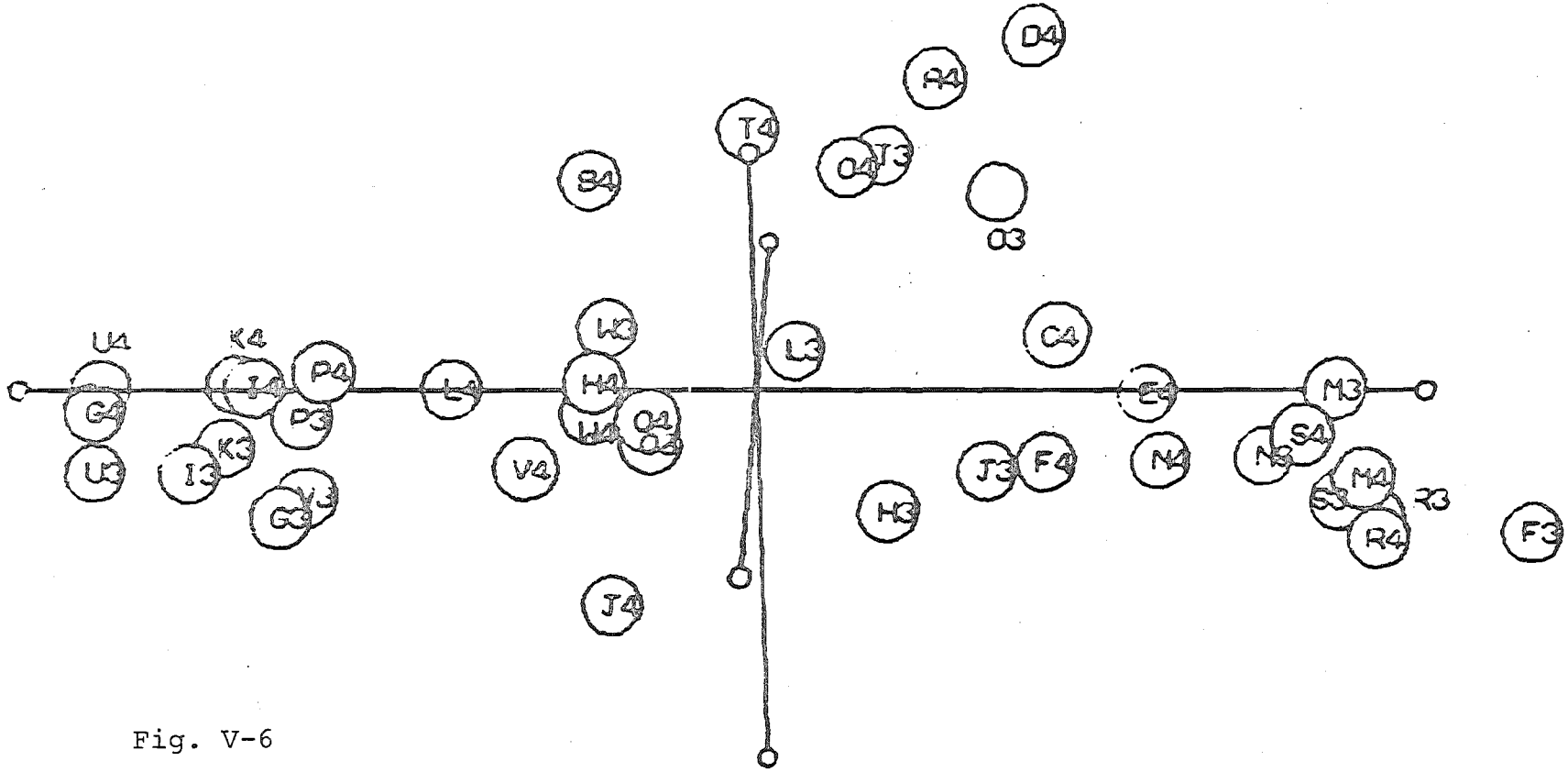

D4
A4
T4
C4
J3
B4
O3
K3
L3
C4
U4
K4
P4
G4
J4
D3
H4
E4
M3
S4
K3
I3
O4
O3
V4
J3
F4
M4
N3
S3
R3
V3
G3
H3
R4
F3
J4

Fig. V-6

Group III

Subjects were tested individually in all experimental sessions. Subjects (8 male, 7 female) were seated as for the previous groups and were issued with instructions and a response booklet. Subjects completed the front page of the response booklet and the experimental sequence began as before. Flasks were presented in the following order: 6, 7, 8, ... 22, 23, 29, 30, ... 45, 46.

Scores were taken from the rating scales and treated as for Group I to generate Euclidean distances for input to MDS. POLYCON was the MDS program used for this analysis.

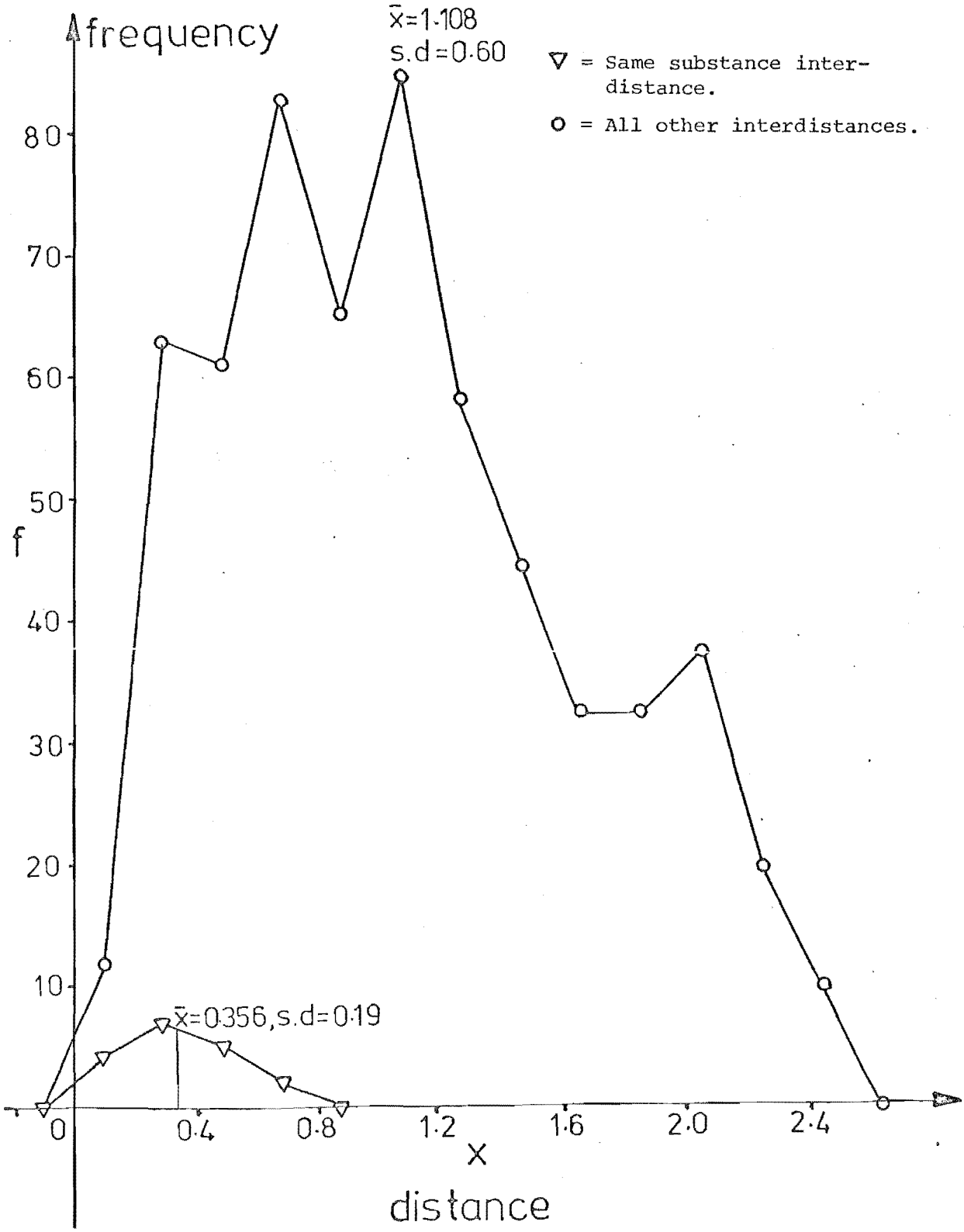
Linear fit was good and stress was low for this solution. Stress was slightly lower than that achieved from the Group I and Group II solutions for the higher dimensionality solutions (See Table V-4). An inter-distance distribution plot (Plot V-3) was again drawn and this showed similar characteristics to those previously discussed. Once again indications were that the metric assumptions for the MDS are justified.

Stimuli are labelled as follows: Stimuli 6 to 23 are F5, G5, H5, ... V5, W5 and stimuli 29 to 46 are F6, G6, H6, ... V6, W6 (See Table V-5).

Consider firstly the plot of Dim I vs Dim II for the 3D solution (Fig. V-7).

Plot V-3

Frequency distribution plot for interdistance measures for Group III.



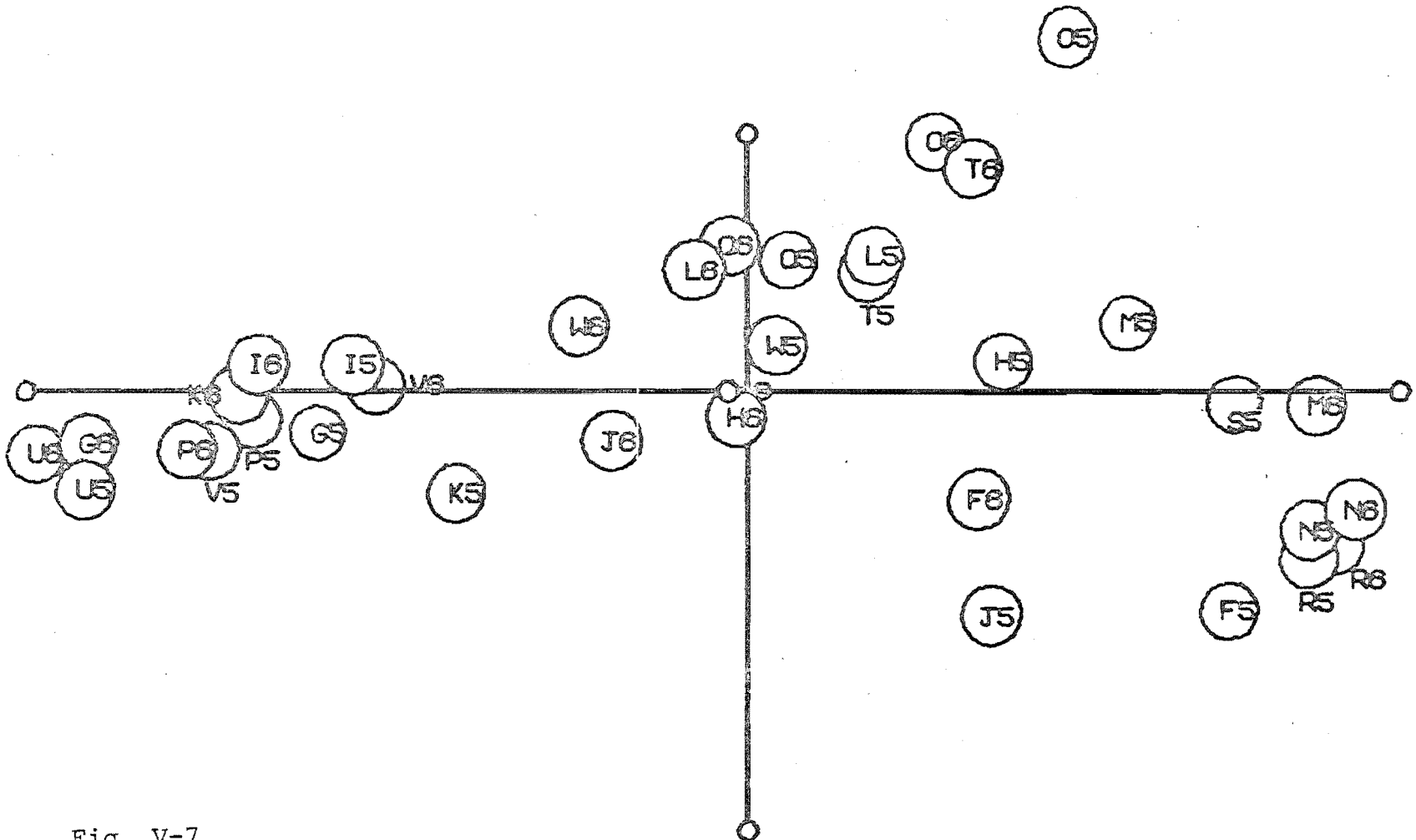

O5
O6
T6
L6
O5
O5
L5
T5
M5
L5
L5
I6
I5
V5
H5
K6
H5
S5
M5
U5
G6
P6
P5
G5
J6
U5
V5
K5
F6
N6
N5
R6
R5
J5
F5

Fig. V-7

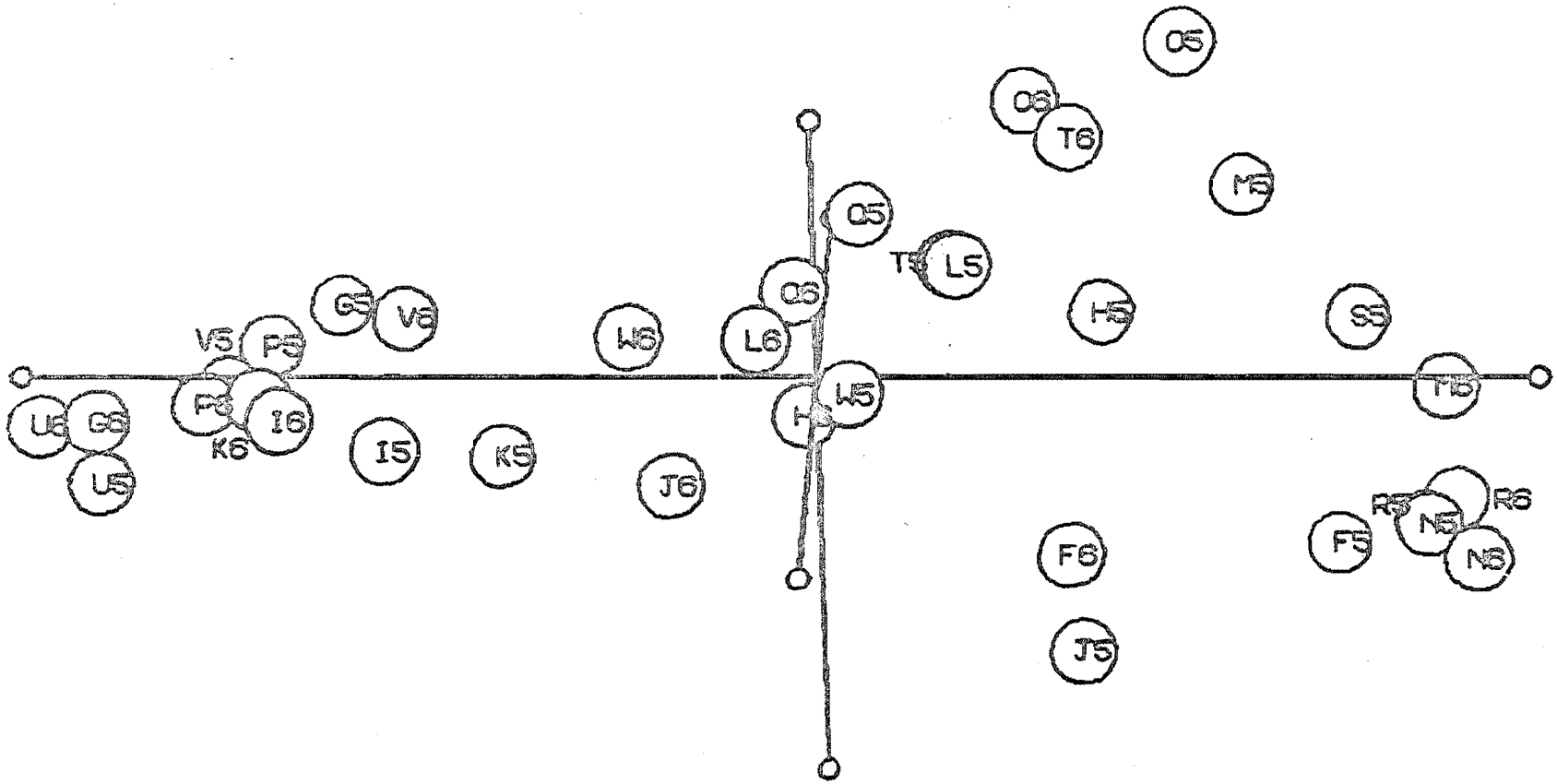

O5
O6
T6
M5
O5
T5
L5
O6
H5
S5
G5
V6
W6
L6
V5
P5
L5
T5
P6
I6
K6
U6
G6
U5
I5
K5
J6
R5
R6
N5
N6
F5
F6
J5

Fig. V-8

A three dimensional view of this plot is seen in Appendix 2. Also included are solutions with 30^{o} rotation of the z axis as before (Fig. V-8 and Appendix 2). Discussion of the clustering in these solutions is seen in Chapter VI.

Group IV

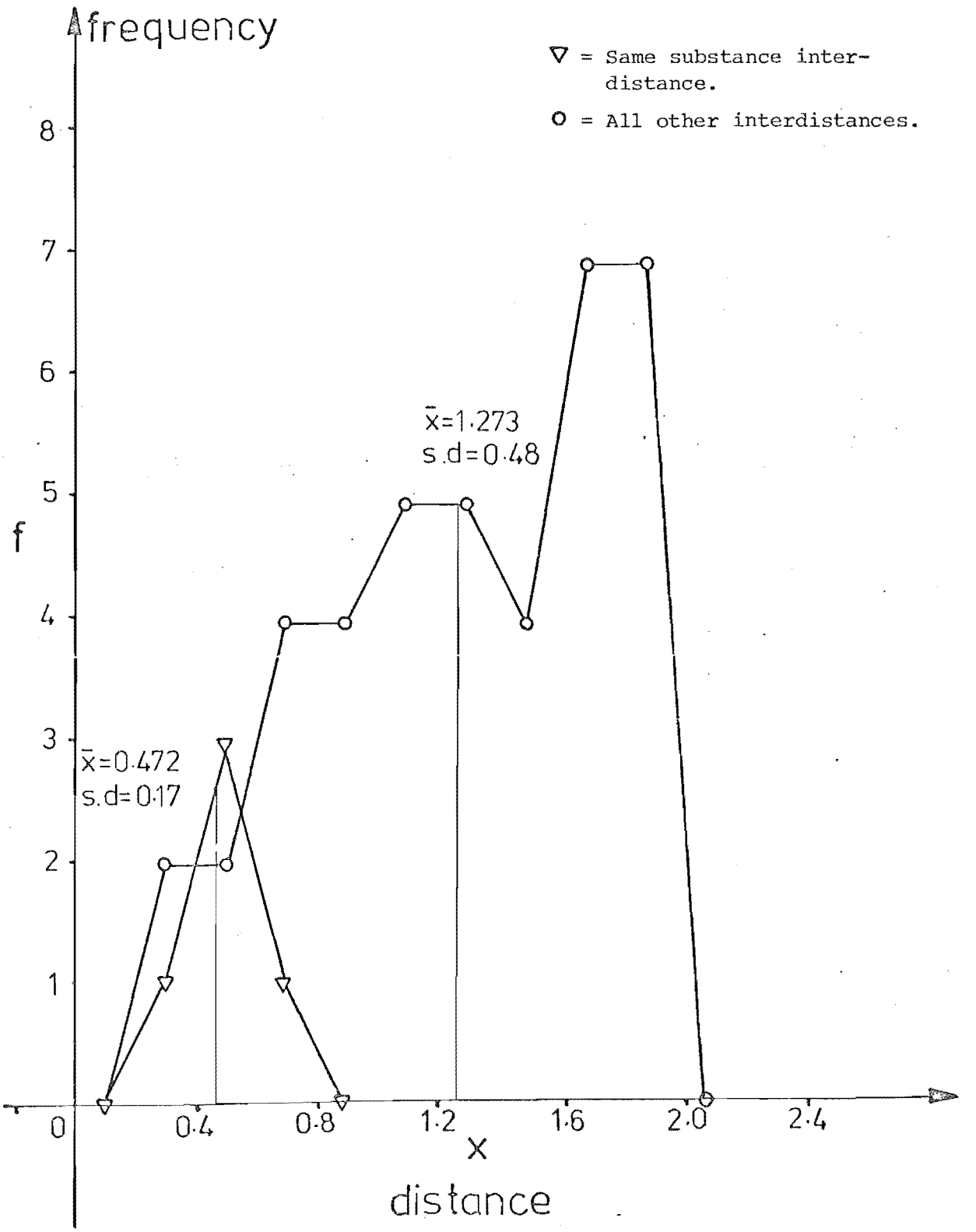
Subjects were treated individually in all experimental sessions. Subjects (9 male, 6 female) were seated as for previous groups and were issued with instructions and a response booklet. Subjects completed the front page requirements as before and the experimental sequence was begun. Flasks were presented in the following order: 1, 2, 3, 4, 5, 24, 25, 26, 27, 28.

Scores were taken from the rating scales and treated as for previous groups to generate Euclidean distances for input to the POLYCON MDS program.

Linear fit was good and stress was low for this solution (See Table V-4). An interdistance distribution plot (Plot V-4) was drawn and this showed similar characteristics to those previously discussed, but now is skewed negatively. This change in distribution form may be consequent solely on the lower number of stimuli involved, it does not in any way invalidate the MDS.

Plot V-4

Frequency distribution plot for interdistance measures for Group IV.



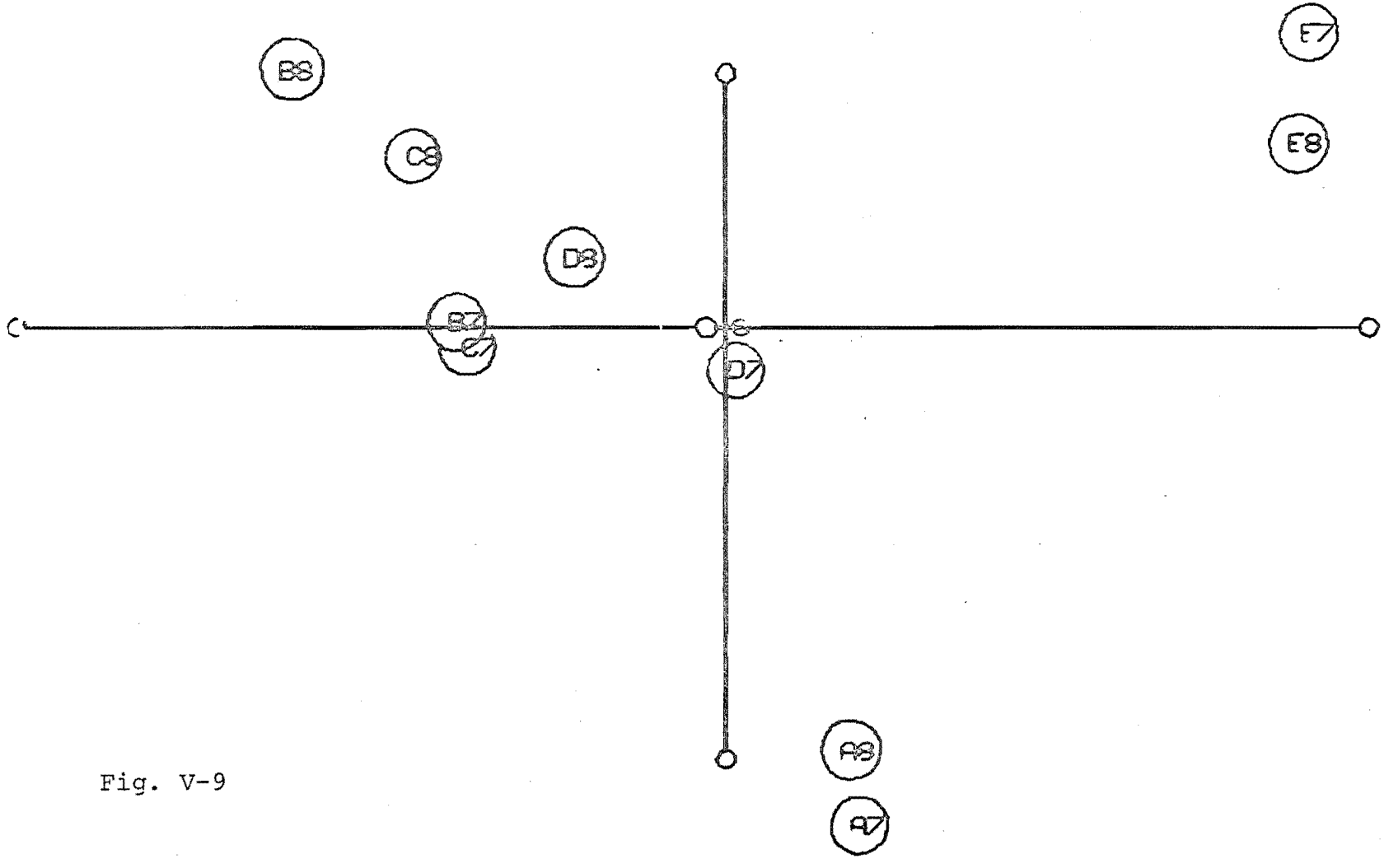


Fig. V-9

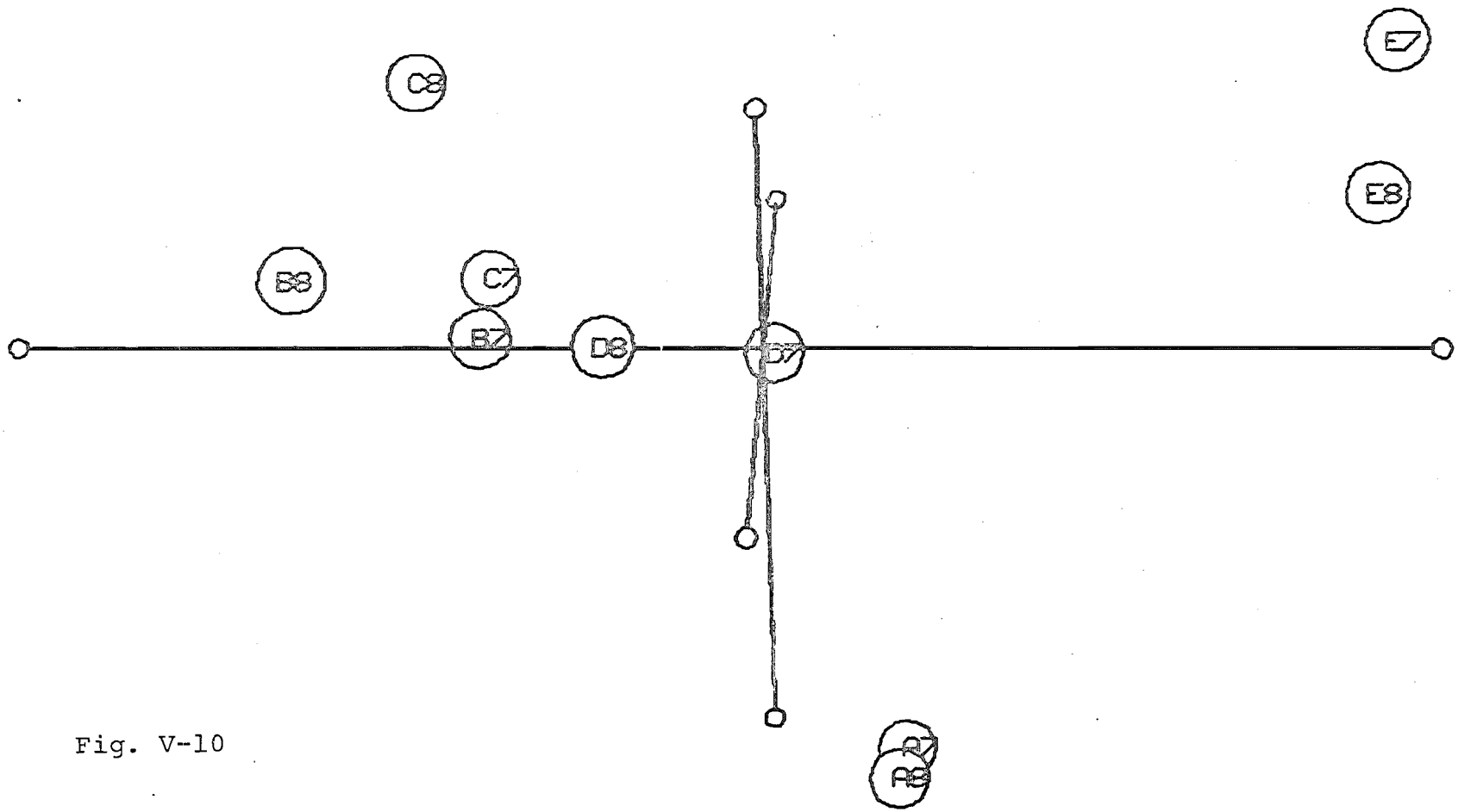


Fig. V-10

Stimuli are labelled as follows: Stimuli 1 to 5 are A7, B7, C7, D7 and E7, stimuli 24 to 28 are A8, B8, C8, D8 and E8 (See Table V-5).

Consider firstly the plot of Dim I vs Dim II for the 3 D solution (Fig. V-9).

A three dimensional view of this plot is seen in Appendix 2. Also included are solutions with 30^{o} rotation of the z-axis as before (Fig. V-10 and Appendix 2). Discussion of the clustering in these solutions is offered in Chapter VI.

CHAPTER SIX

MAJOR STUDY - DISCUSSION

The presentation order for stimuli within any of the four experimental groups for this study may be conveniently considered in two sections. The flasks numbered 1 to 23 contain the odour stimuli in their first presentation and the flasks 24 to 46 contain the same stimuli in a second presentation. The ordering of stimuli for each presentation is randomised and differs for the two presentation orders. It is useful to be able to compare, via some scaling analysis, the within group comparisons for the first and second presentations, as such a comparison will reveal any order effects, other than a simple linear transformation, which may occur in the relative perception of the odours. Such comparisons thus constitute a measure of reliability of the data. For this reason the within group comparisons will be considered first in this chapter.

Some direct comparisons are possible between equivalent presentations of different experimental groups. For example, the presentation of the first eighteen "structural" stimuli to groups II and III is such a case. This can provide some inter-subject reliability measure. Hence, some between group comparisons will be considered next.

The results for each of the groups I, II and III suggest some clustering of each of the three molecular

types (bornane derivatives, norbornane derivatives and cyclohexane derivatives). It is necessary to consider this clustering with regard to the topology of structure within clusters. Within cluster analysis for each of the structurally related groups of stimuli is considered in some detail for the group I solution and related consideration given to the other group solutions.

The effect of the "anchor" series on the distribution of the structurally related compounds is examined, because this can show whether or not the inclusion of the "anchor" series would have any effect on the distributions of the "structural" compounds in this experiment.

The chapter will conclude with some general comments on dimension labelling. The relation of this work to other work in the field is explored in Chapter VIII.

Within Group Comparisons

1. Group I.

The distribution may be considered first in relation to the two separate presentations of the stimuli. It is necessary to consider whether or not there are any obvious differences in the distribution of the stimuli A1, B1, C1, ... V1, W1 and the stimuli A2, B2, C2, ... V2, W2 in the MDS of subject responses (see Fig. V-3 and Fig. V-4 as well as Appendix 2).

There does not appear to be any obvious difference

in the distributions for each of the presentation orders. In some cases a relatively large distance is seen between successive presentations of the same stimulus (e.g. J1 and J2, O1 and O2) but in the majority of cases the same stimuli, on separate presentations, lie close together (e.g. R1 and R2, Q1 and Q2, U1 and U2). A frequency polygon of the distance between the same stimuli in different presentations has been presented in the previous chapter (Plot V-1). This gives a comparison of the above plot with that of the interstimuli distances between different stimuli. The mean distance between the same stimuli on the different presentations was 0.372 (Standard Deviation 0.151) whilst that between different stimuli was 1.118(Standard Deviation 0.582). This represents a significant difference (Behrens-Fisher test, $p < .05$). Thus the distance between different stimuli is much greater than between the same stimulus on different presentations.

There are no apparent differences in the distribution of stimuli for first and second presentations which could be directly attributed to presentation order so consideration may now be made of the overall pattern of the distribution.

(i) Structurally related stimuli (F1, G1, H1, ... V1, W1 and F2, G2, H2, ... V2, W2).

There are three clusters of stimuli which effectively group the stimuli as to molecular type (bornane

derivatives, norbornane derivatives and cyclohexane derivatives). The cluster in the upper right hand corner contains the stimuli:

F1 and F2	(1R,2R,4R)-Born-2-yl acetate
M2 and M2	Bornane
N1 and N2	(1R,2S,3R,4S)-2,3-Epoxybornane
R1 and R2	(1R,4R)-Camphor
S1 and S2	(1R,2R,4R)-Bornan-2-ol.

The stimuli J1 and J2 ((1R,4R)-Born-2-ene) lie relatively close to this cluster and may be considered with that cluster in the "within cluster" section of this chapter.

The stimuli E1 and E2 (1,8-Cineole) which are also in the cluster are from the anchor series and represent camphoraceousness in Amoore's studies (Amoore, 1970).

The second cluster is situated around the origin of the Dim.I axis and to the negative side of the Dim.II axis. The cluster (excluding the anchor stimuli present) comprises the stimuli:

H1 and H2	Cyclohexanol
L1 and L2	Epoxycyclohexane
Q1 and Q2	Cyclohexane
T1 and T2	Cyclohexyl acetate
W1 and W2	Cyclohexanone

In addition the stimuli O1 and O2 (exo-norborn-2-yl acetate) are also present. However, this appears to be an exception to the rule and this will be further discussed in the "within cluster" section of this chapter. This cluster contains all of the cyclohexane derivatives except cyclohexene.

The third cluster lies to the extreme left of the Dim.I axis and contains mostly norbornane derivatives. The cluster contains the following stimuli:

G1 and G2	Norcamphor
K1 and K2	2,3-exo-Epoxynorbornane
P1 and P2	Norbornane
U1 and U2	Norborn-2-ene
V1 and V2	exo-Norbornan-2-ol.

In addition the stimuli I1 and I2 (Cyclohexene) are present in this cluster.

The Fig. V-4 shows the same solution rotated 30^{o} out of the page along the Dim.III axis. This solution gives some indication of the relative positions for those stimuli which were obscured in the Fig. V-3.

Overall, it would appear that presentation order has little effect on the topology of the scaling solution achieved, which is the desired result. Three groups of stimuli are observed which are basically those of (i) bornane derivatives, (ii) norbornane derivatives and (iii) cyclohexane derivatives. There are two major exceptions

to this rule (cyclohexene and exo-norborn-2-yl acetate) and these exceptions will be discussed in a later section of this chapter.

(ii) The anchor stimuli (A1, B1, C1, D1, E1 and A2, B2, C2, D2, E2).

These stimuli show reliability in positioning for the two presentations. The stimuli A1 and A2 (Isoamyl acetate) and D1 and D2 (Eugenol) are situated on the positive side of the Dim.I axis and the negative side of the Dim.II axis. The stimuli B1 and B2 (Methylpropionate) and C1 and C2 (n-Propanol) are situated around the origin of the Dim.I axis and slightly to the negative side of the Dim.II axis. The stimuli E1 and E2 (1,8-Cineole) are situated to the positive side of both Dim.I and Dim.II.

2. Group II.

The distribution may be considered first in relation to the two separate presentations of the stimuli. It is necessary to consider whether or not there are any obvious differences in the distribution of the stimuli F3, G3, H3, ... V3, W3 and the stimuli A4, B4, C4, ... V4, W4 in the scaling solutions (see Fig. V-5, Fig. V-6 and Appendix 2).

Once again there does not appear to be any obvious difference in the distributions for each of the present-

ation orders. The solution gained is rotated through 180^{o} on the Z-axis if compared with the previous solutions. Once again there are some cases in which the distance between same stimuli on separate presentations is relatively large (e.g. J3 and J4, L3 and L4) but in the majority of cases same stimuli lie close together (e.g. R3 and R4, M3 and M4, P3 and P4). A frequency polygon of the distance between same stimuli in different presentations has been presented in Chapter V (Plot V-2). This gives a comparison of the plot of interdistances for same stimuli with the plot of interdistances of unlike stimuli. The mean distance between the same stimuli on the different presentations was 0.398 (Standard Deviation 0.233) whilst that between different stimuli was 1.116 (Standard Deviation 0.560). Once again the distance between different stimuli is much greater than the distance between same stimuli on different presentations.

There are no apparent differences in the distribution of stimuli for first and second presentations which are directly attributable to presentation order so consideration may now be made of the overall pattern of the distribution.

(i) Structurally related stimuli (F3, G3, H3, ... V3, W3 and F4, G4, H4, ... V4, W4).

Again there are three clusters of stimuli which effectively group as to molecular type (bornane derivatives,

norbornane derivatives and cyclohexane derivatives). The cluster in the lower right hand corner contains the stimuli:

F3 and F4	(1R,2R,4R)-Born-2-yl acetate
M3 and M4	Bornane
N3 and N4	(1R,2S,3R,4S)-2,3-Epoxybornane
R3 and R4	(1R,4R)-Camphor
S3 and S4	(1R,2R,4R)-Bornan-2-ol.

The stimuli J3 and J4 (1R,4R)-Born-2-ene) lie relatively close to this cluster and may be considered with that cluster in the "within cluster" section of this chapter. This solution has an identical cluster content to that of Fig. V-3 in the Group I solution but the spread of the stimuli is broader.

The second cluster is situated around the origin of the Dim.I axis and to the positive side of the Dim.III axis. The cluster (excluding the anchor stimuli) comprises the stimuli:

H3 and H4	Cyclohexanol
L3 and L4	Epoxycyclohexane
Q3 and Q4	Cyclohexane
T3 and T4	Cyclohexylacetate
W3 and W4	Cyclohexanone.

In addition the stimuli O3 and O4 (exo-norborn-2-yl acetate) are also present; this will be discussed later in this

chapter. This cluster contains all of the cyclohexane derivatives except cyclohexene.

The third cluster lies to the extreme left of the Dim.I axis and contains mostly norbornane derivatives. The cluster containes the following stimuli:

G3 and G4	Norcamphor
K3 and K4	2,3-exo-Epoxynorbornane
P3 and P4	Norbornane
U3 and U4	Norborn-2-ene
V3 and V4	exo-Norbornan-2-ol.

In addition the stimuli I3 and I4 (Cyclohexene) are present in this cluster.

The Fig. V-6 shows the same solution rotated 30^{o} out of the page along the Dim.III axis. This solution gives some indication of the relative positions for those stimuli which were obscured in the Fig. V-5.

Overall it would appear once again that presentation order has little observable effect on the solution achieved. Three groups of stimuli are again observed which are basically those of (i) bornane derivatives, (ii) norbornane derivatives and (iii) cyclohexane derivatives. The same stimuli were exceptions to the rule, in this scaling solution. The reasons for this exception will be examined.

There is a marked similarity in the solutions gained for Group I and Group II subjects. In both cases

three main clusters were evident and these are arranged in a similar spatial order. This is some evidence for the reliability of the technique and further evidence will be presented later.

(ii) Anchor stimuli (A4, B4, C4, D4 and E4)

The stimuli showed similar positioning to that achieved in the Group I solution. The stimuli A4 (Isoamyl-acetate), B4 (Methylpropionate), C4 (n-Propanol) and D4 (Eugenol) were associated with the cyclohexane derivative cluster. However, the stimulus C4 was a little further to the right along the Dim.I axis than the previous solution. The stimulus E4 (1,8-Cineole) was again found in the bornane derivative cluster.

3. Group III.

The two separate presentations of the stimuli will be considered first. We examine whether or not there are any obvious differences in the distribution of the stimuli F5, G5, H5, ... V5, W5 and the stimuli F6, G6, H6, ... V6, W6 in the scaling solutions (see Fig. V-7, Fig. V-8 and Appendix 2).

Once again there does not appear to be any obvious difference in the distributions for each of the present-ation orders. The solution is in the same orientation as the Group II solution, rotated through 180° on the Z-axis

compared with the Group I solution. Again there are some cases in which the distance between same stimuli on separate presentations is relatively large (e.g. J5 and J6, H5 and H6) but in the majority of cases two presentations of the same stimulus lie close together (e.g. N5 and N6, R5 and R6, U5 and U6). A frequency polygon of the distance between same stimuli in different presentations has been presented in Chapter V (Plot V-3). This gives a comparison of the plot of interdistances for same stimuli with the plot of interdistances of unlike stimuli. The mean distance between the same stimuli on the different presentations was 0.356 (Standard Deviation 0.192) whilst that between different stimuli was 1.108 (Standard Deviation 0.600). Once again the distance between different stimuli is much greater than the distance between same stimuli on different presentations.

There are no apparent differences in the distribution of stimuli for first and second presentations which are directly attributable to presentation order so consideration may be made directly of the overall pattern of the distribution.

Only structurally related stimuli were used in this experiment. The structurally related stimuli were F5, G5, G5, ... V5, W5 and F6, G6, H6, ... V6, W6.

Again there are three clusters of stimuli which effectively group as to molecular type (Bornane derivatives, Norbornane derivatives and Cyclohexane derivatives). The cluster in the lower right hand corner

contains the stimuli:

F5 and F6	(1R,2R,4R)-Born-2-yl acetate
M5 and M6	Bornane
N5 and N6	(1R,2S,3R,4S)-2,3-Epoxybornane
R5 and R6	(1R,4R)-Camphor
S5 and S6	(1R,2R,4R)-Bornan-2-ol.

The stimuli S5 and S6 lie on the same coordinates so only S5 is plotted. The stimuli J5 and J6 ((1R,4R)-born-2-ene) lie relatively close to this cluster and may be considered with the cluster in the "within cluster" section of this chapter. This solution has identical cluster content to those achieved for Groups I and II but here the spread is somewhat broader for the bornane cluster.

The second cluster is situated around the origin of the Dim.I axis and to the positive side of the Dim.III axis. The cluster contains the stimuli:

H5 and H6	Cyclohexanol
L5 and L6	Epoxycyclohexane
Q5 and Q6	Cyclohexane
T5 and T6	Cyclohexylacetate
W5 and W6	Cyclohexanone.

In addition the stimuli O5 and O6 (exo-norborn-2-yl acetate) are also present; this will be discussed later in this chapter. This cluster contains all of the cyclohexane

derivatives except cyclohexene.

The third cluster lies to the extreme left of the Dim.I axis and contains mostly norbornane derivatives. The cluster contains the following stimuli:

G5 and G6	Norcamphor
K5 and K6	2,3-exo-Epoxynorbornane
P5 and P6	Norbornane
U5 and U6	Norborn-2-ene
V5 and V6	exo-Norbornan-2-ol.

In addition the stimuli I5 and I6 (cyclohexene) are present in this cluster. This cluster contains all the norbornane derivatives except exo-norborn-2-yl acetate.

The Fig. V-8 shows the same solution rotated 30^{o} out of the page along the Dim.III axis. This solution gives some indication of the relative positions for those stimuli which were obscured in Fig. V-7.

Overall it would appear once again that presentation order has little observable effect on the solution achieved. Three groups of stimuli are again observed with the same exceptions to the cluster patterns. Again there is a marked similarity with the previous solutions which lends further support to the reliability of the technique.

4. Group IV

Again the two separate presentations of the stimuli

will be considered first: differences in the distribution of the stimuli A7, B7, C7, D7, E7 and the stimuli A8, B8, C8, D8, E8 in the scaling solutions (see Fig. V-9, Fig. V-10 and the Appendix 2), are examined.

Once again there does not appear to be any obvious difference in the distributions for each of the presentation orders. In all cases the distance between same stimuli is relatively small. The frequency polygon of the distance between same stimuli in different presentations (Plot V-4) gives a comparison with the plot of interdistances for unlike stimuli. Patterns emerge similar to those discussed previously. The mean distance between same stimuli on the different presentations was 0.472 (Standard Deviation 0.171) whilst that between different stimuli was 1.273 (Standard Deviation 0.478).

There are no apparent differences in the distribution which are directly attributable to presentation order so consideration may now be made of the overall pattern of the distribution.

Only anchor stimuli were used in this experiment. The anchor stimuli were A7, B7, C7, D7, E7 and A8, B8, C8, D8, E8.

Here the stimuli A7 and A8 (Isoamylacetate) are found to the positive side of Dim.I and to the far negative side of Dim.II. The stimuli B7 and B8 (Methylpropionate), C7 and C8 (n-Propanol) and D7 and D8 (Eugenol) all lie around the origin and so the negative side of the Dim.I axis and to the slightly positive side of the Dim.II

axis. The remaining stimuli E7 and E8 (1,8-Cineole) lie to the positive sides of both axes. This distribution pattern is in alignment with those achieved for Group I and Group II with the exception that the stimuli D7 and D8 would have been expected to lie closer to the stimuli A7 and A8.

Overall it would appear that presentation order has little observable effect on the solution achieved. There is a marked similarity with the previous solutions which lends further support for the reliability of the technique.

Between Group Comparisons

A number of direct comparisons of this type are possible with this experimental design. The first to be considered is the comparison between the second presentation for Group I subjects with the second presentation for Group II subjects. The second of these comparisons is between the first presentation for Group II subjects and the first presentation for Group III subjects. Another possibility will only be touched on briefly and that is the comparison between the first five stimuli for the first presentation to Group I and the first five stimuli presented to Group IV.

1. Comparison of the second presentation to Groups I and II.

Here all 23 stimuli are presented in the same randomised order to both groups of subjects. It is of interest to consider any differences in the resulting distributions of A2, B2, C2, ... V2, W2 and A4, B4, C4, ... V4, W4. A separate plot (Fig. VI-1) has been prepared for this purpose. Here the stimuli A2, B2, C2, ... V2, W2 are plotted directly and the stimuli A4, B4, C4, ... V4, W4 are rotated through 180° to enable direct comparison of the solutions. The plot Fig. VI-2 is the same solution rotated 30° out of the page along the Z-axis and as for previous cases three dimensional plots are presented in Appendix 2.

There does not appear to be any obvious difference between the two distributions. There may even be a slightly shorter interstimuli distance for same stimuli than is the case for the intragroup comparisons, suggesting that intersubject reliability may be even better than intrasubject reliability. It is virtually impossible to test this point quantitatively without setting up a model of the distribution of expected distances in the scaling space.

The overall pattern of the distributions is still clearly seen. There are the three clusters of structurally rotated compounds (Bornane derivatives, Norbornane derivatives and Cyclohexane derivatives) and the anchor stimuli are distributed as before.

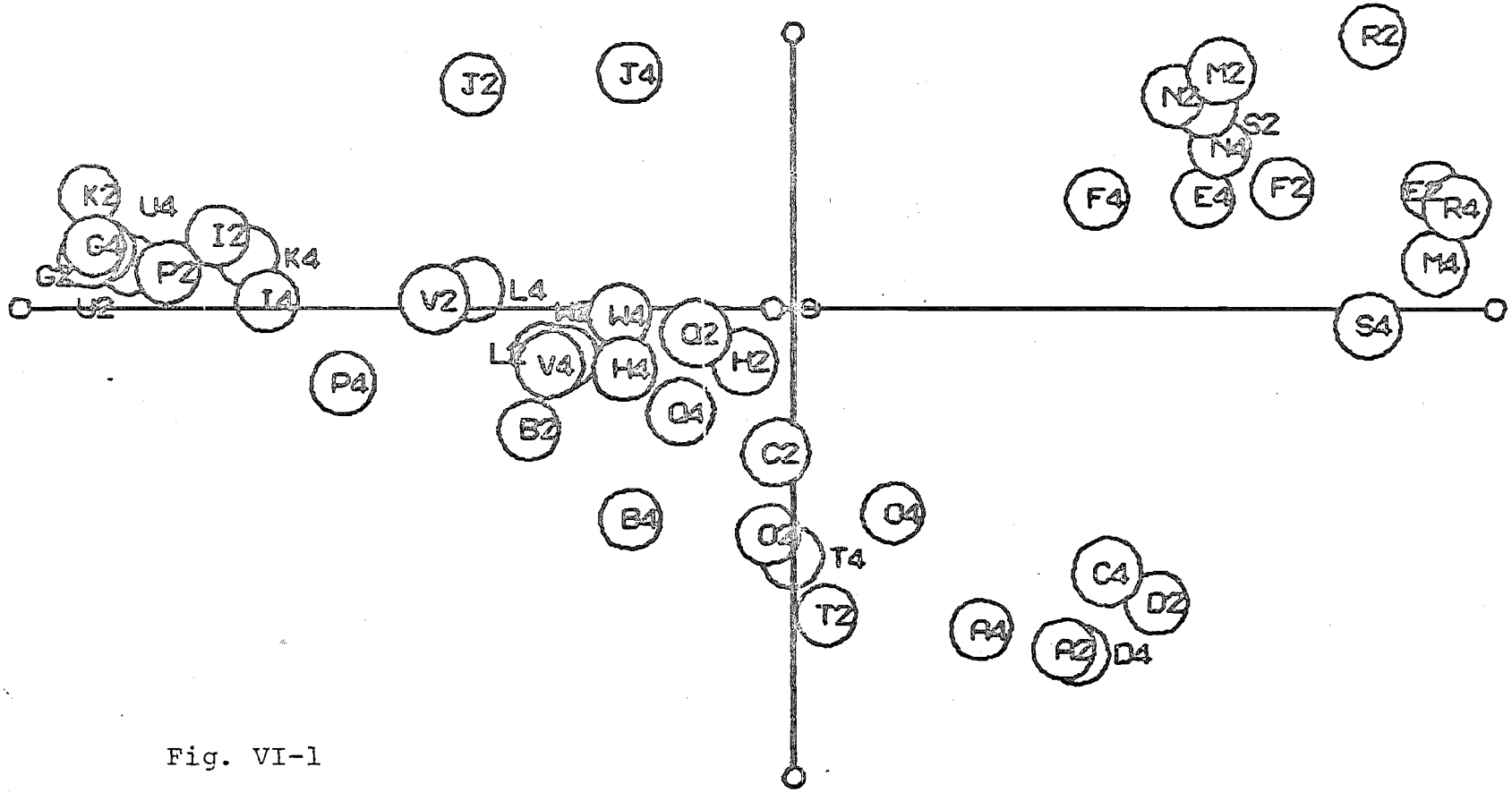

J2
J4
R2
M2
N2
S2
N4
F4
E4
F2
E2
R4
M4
K2
U4
I2
G4
K4
G2
P2
I4
U2
V2
L4
W4
O2
H2
L2
V4
H4
O4
P4
B2
C2
B4
O3
O4
T4
T2
C4
D2
P4
P2
D4
S4

Fig. VI-1

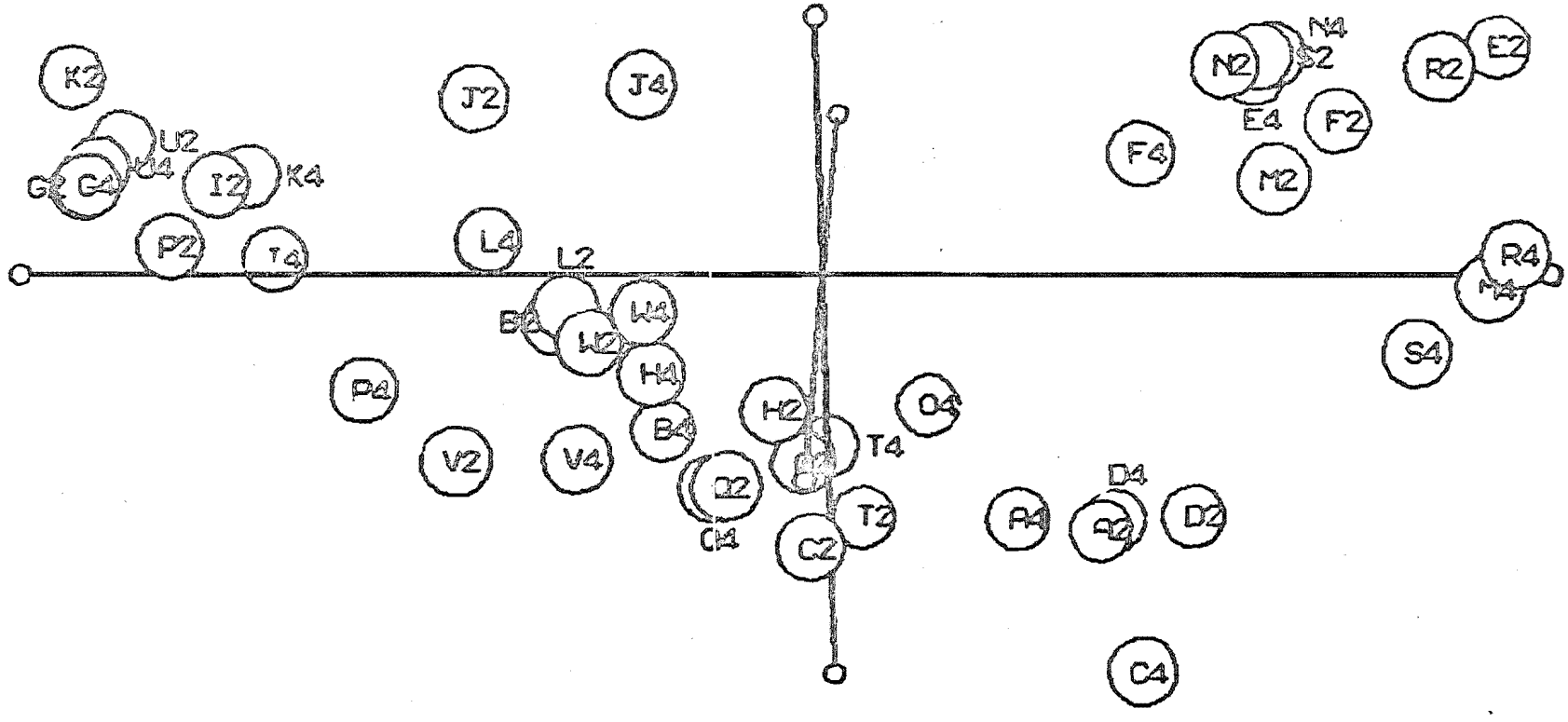

K2
J2
J4
N4
N2
S2
R2
E2
U2
K4
I2
K4
E4
F2
F4
M2
P2
T4
L4
L2
R4
S4
P4
H4
H2
O4
T4
V2
V4
B4
D2
C4
T2
D4
P4
D2
C2
C4

Fig. VI-2

2. Comparison of the first presentation to Groups II and III.

There the 18 structurally rotated stimuli are presented in the same randomised order to both groups of subjects. It is of interest to consider any differences in the resulting distributions of F3, G3, H3, ... V3, W3 and F5, G5, H5, ... V5, W5. A separate plot (Fig. VI-3) has been prepared for this purpose. Here both sets of stimuli have been plotted directly. The plot Fig. VI-4 is the same solution rotated 30^{o} out of the page along the z-axis and as for previous cases three dimensional plots are presented in Appendix 2.

There does not appear to be any obvious difference between the two distributions although the central cluster (cyclohexane derivatives) does appear to be more spread than in the previous scaling solutions.

The overall pattern of the distributions is still clearly seen. There are three clusters of struturally related stimuli (Bornane, Norbornane and Cyclohexane derivatives) but in this case it would appear that the intersubject homogeneity is weaker than in the previous case.

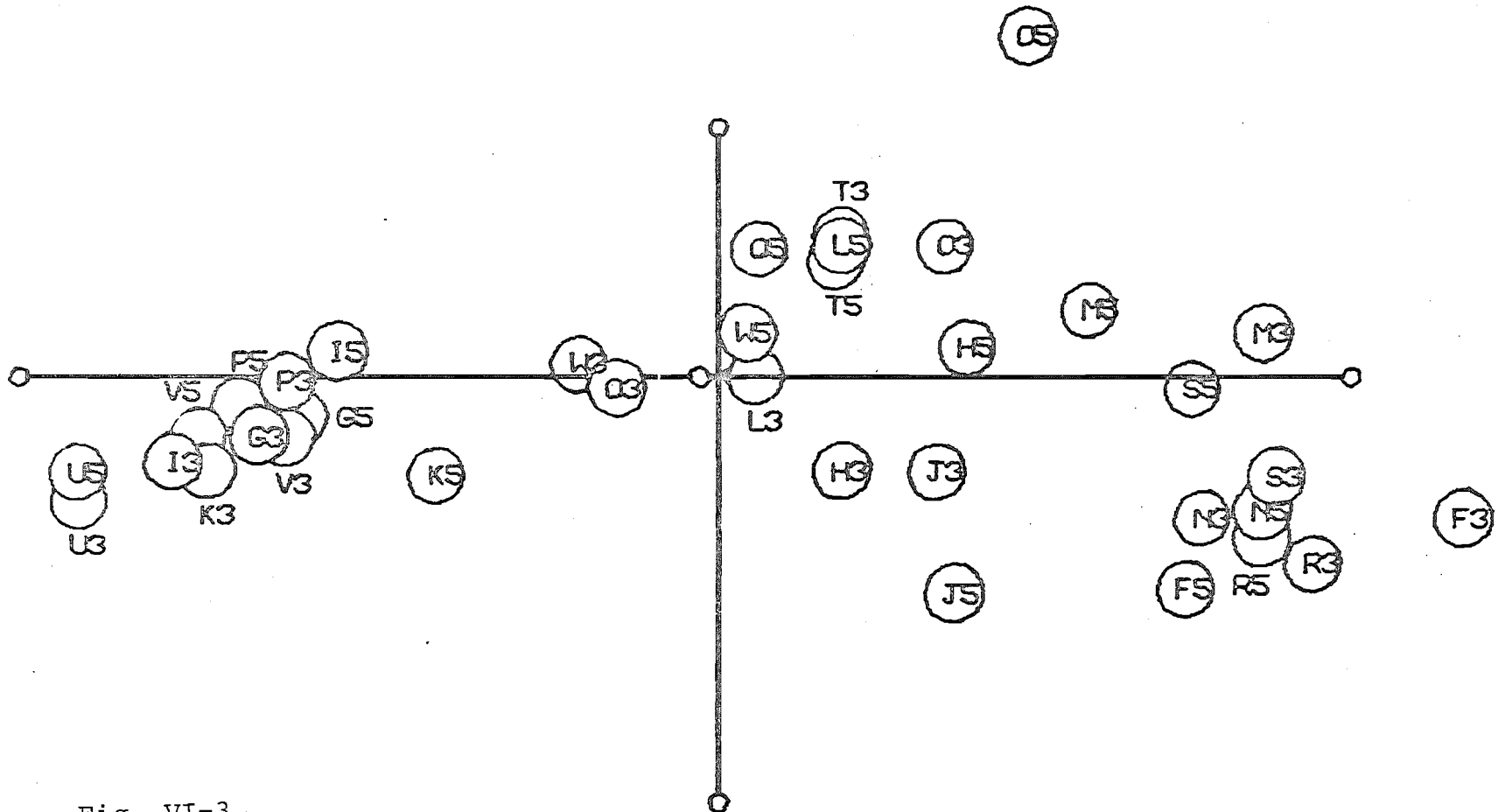

C5
T3
C5
L5
C3
T5
M5
M3
W5
H5
I5
P5
P3
W5
G5
L3
S5
G3
I3
V3
K3
K5
H3
J3
S3
N3
N5
F3
U5
U3
R3
J5
F5
R5

Fig. VI-3

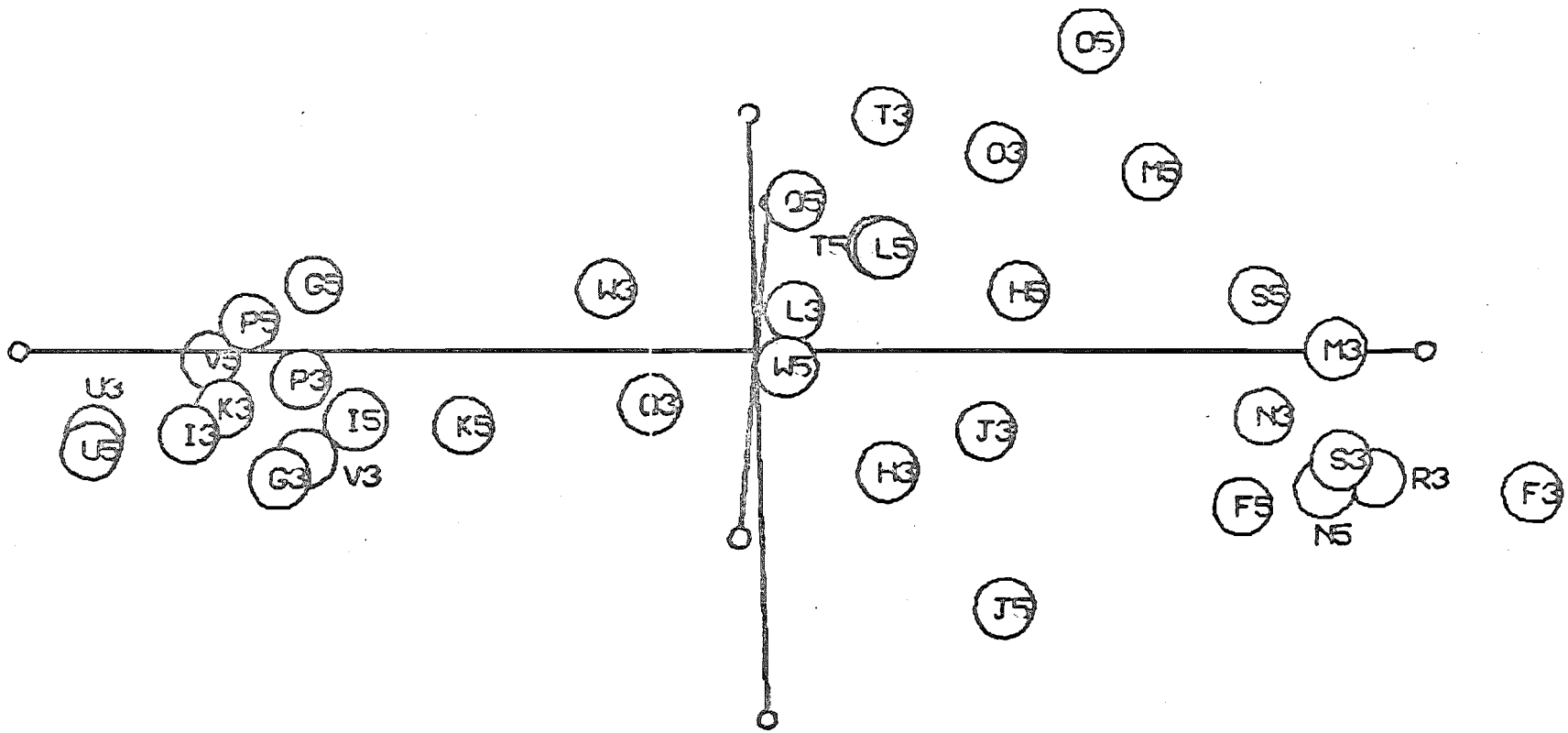

O5
T3
O3
M5
O5
T5
L5
G5
K3
H5
S5
P5
L3
M3
V5
W5
P3
U3
K3
O3
N3
I5
K5
J3
S3
R3
I3
U5
G3
V3
H3
F3
F5
N5
J5

Fig. VI-4

3. Comparison of the first five stimuli from Groups I and IV.

Here the 5 anchor stimuli are compared for two subject groups. No special plots have been drawn in this case as simple comparisons may be made from the appropriate plots (Fig. V-3 and Fig. V-9). Very similar patterns are observed for the two distributions even though one of them is embedded in the larger distribution. There is no obvious difference between the two distributions.

Overall we have seen that the intersubject reliability is at least as good as the intrasubject reliability which was covered in the previous section.

Within Cluster (Structurally Related Stimuli)

The solutions for Groups I, II and III all gave three major clusters which correspond to the three molecule types used for this study (Bornane derivatives, Norbornane derivatives and Cyclohexane derivatives). Some exceptions to this have been noted previously and these will now be considered here along with some general comments on the clustering. In addition separate analyses have been made for each of the molecule types on both presentations to Group I and the POLYCON MDS solutions for these are presented in this section. In each of the cases the data cards for each of the molecule types were treated separately, euclidean distances were generated and the half matrix of distances was used as direct input

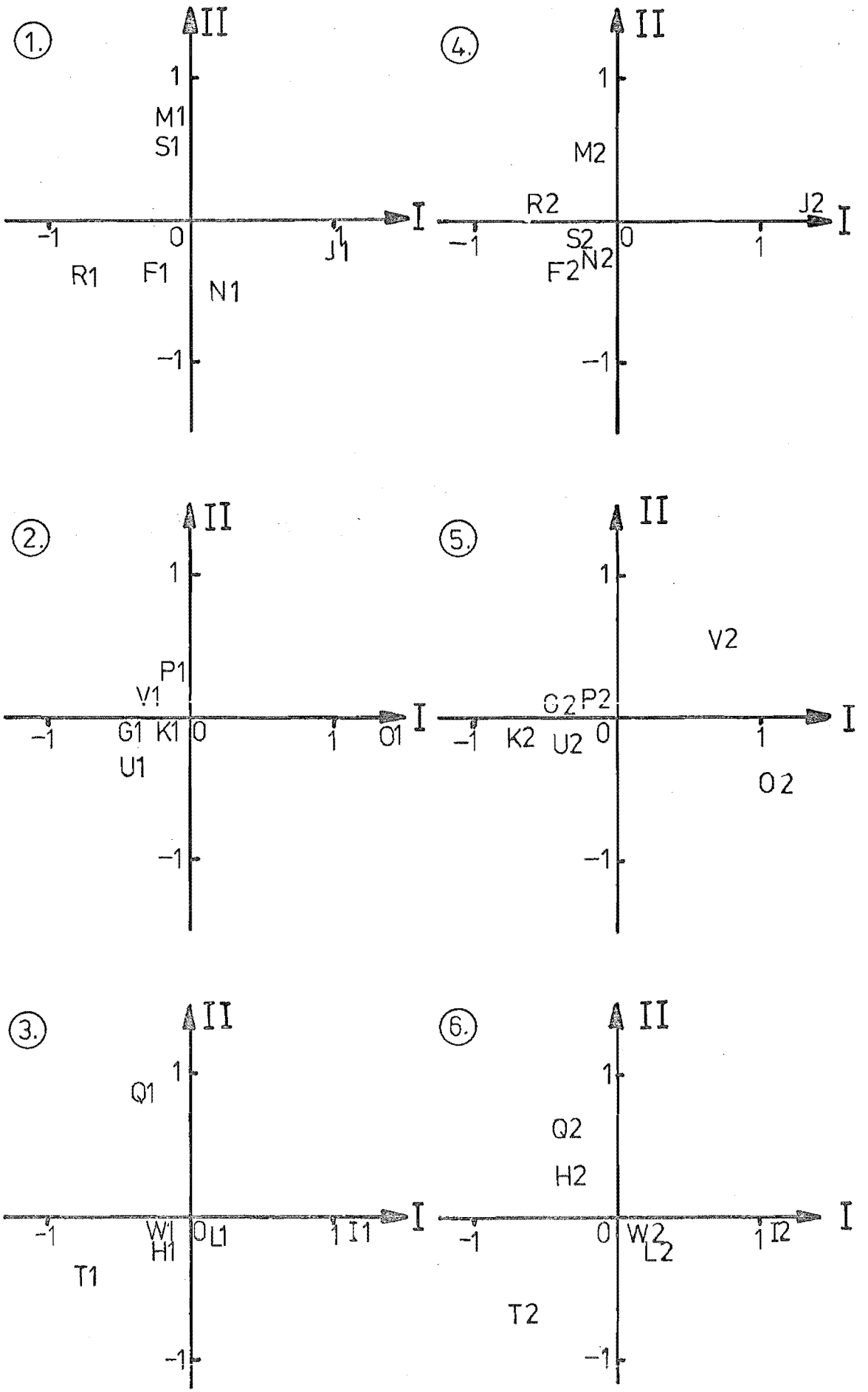
to POLYCON.

Some general observations will be presented first which refer to the solutions for Groups I-III (Figs. V-3,5,7). In each case the bornane cluster lies to the positive side of the Dim.I axis and the stimuli to the far left (negative) of the cluster are the J stimuli i.e. the series J1, J2, ... J6 ((1R,4R)-born-2-ene). The other distinguishing feature of the cluster is a tendency for the R stimuli ((1R,4R)-camphor) and the F stimuli ((1R,2R,4R)-born-2-yl acetate) to lie to the extreme right (positive) side of Dim.I and to the extreme polar end of Dim.II.

The cyclohexane cluster lies in the centre of the distribution in each of the group solutions. The exception in this case is the presence of the stimuli O (exo-norborn-2-yl acetate) to the far right of this cluster; all other stimuli are cyclohexane derivatives. The stimuli T (cyclohexylacetate) also lie to the extreme right of the cluster for each of the group solutions. From these overall solutions no detectable pattern is seen for the other stimuli. Consideration of the I stimuli (cyclohexene) shows that these stimuli always lie to the extreme left of the cyclohexane cluster.

The norbornane cluster lies to the extreme left of the distribution and contains all norbornane stimuli with the exception of the acetate which has been mentioned. The cluster is lightly bunched with perhaps the major distinguishing feature being the presence of the G stimuli

Fig. VI-5


1.
II
1
M1
S1
I
-1
0
1
J1
R1
F1
N1
-1
4.
II
1
M2
R2
J2
I
-1
S2
0
1
F2
N2
-1
2.
II
1
P1
V1
I
-1
G1
K1
0
1
O1
U1
-1
5.
II
1
V2
G2
P2
I
-1
K2
U2
0
1
O2
-1
3.
II
1
Q1
I
-1
W1
H1
0
L1
1
I1
T1
-1
6.
II
1
Q2
H2
I
-1
0
W2
L2
1
I2
T2
-1

(norcamphor) and U stimuli (norborn-2-ene) to the far left of the clusters.

Overall it would appear that the clusters show a tendency for the alkenes to lie to the far left of Dim.I and the acetates to lie to the far right of Dim.I. The alkenes were, in general, reported as being most unpleasant while the acetates were reported ad being most pleasant. The dimension pleasantness-unpleasantness commonly emerges as dominant in psychophysical multi-dimensional scalings of very diverse sets of odours, so this is not a surprising finding.

The 2D solutions (Fig. VI-5) for each of the molecule types from the Group I solutions bear out these generalizations. They demonstrate once again the reliability of the procedure as the pairs of solutions for the same stimuli demonstrate. The relative positioning of the acetates and alkenes to the cluster is again apparent.

Effect of Anchor series on the Structurally Related Compounds

If we first consider the within group case we see that for Group II the first presentation has no exposure to the anchor series while the second presentation is preceded by the anchor series. However, the distribution for the first 18 stimuli (F3, G3, H3, ... V3, W3) does not differ significantly from the 18 structurally related stimuli in the second presentation (F4, G4, H4, ... V4, W4).

Thus, it would appear that the presence of the anchor series has very little observable effect in this case.

If we now consider the between groups case where the first presentation to Groups I and II are compared. Here again one group has the anchor series present and the other has not.

However, once again there is no observable difference in the distributions of the structurally related stimuli so it would appear that the presence of the anchor series has negligible effect.

Summary

In this chapter we have seen that the reliability of this procedure is good both for within group measures and between group measures. There is no observable and non-trivial difference in the topology of the distributions of the structurally related stimuli in any of the different presentation orders or for any of the subject groups.

Three clusters were formed for the structurally related stimuli which were representative of the three molecule types (Bornane, Norbornane and Cyclohexane). There were two exceptions to this and these stimuli were cyclohexene and exo-norborn-2-yl acetate.

If we look at the internal structure of the clusters we see that these exceptions fit the general pattern. Within clusters we tend to find the extreme

left of the cluster to be occupied by an alkene and the extreme right of the cluster to be occupied by an acetate. In both cases, with the exceptions mentioned, the placing is an extreme form of this rule. The other stimuli were clustered so close within the clusters that no general comments can be made of their distribution.

The presence of the anchor series had no observable effect on the distribution of the structurally related compounds. In addition the positioning of the anchor stimuli were consistent both within and between groups.

As far as dimension labelling goes it would be safe to label Dim.I as hedonic but no reliable label, either psychological or clinical, could be given to the other dimensions.

However, it is possible to establish reliability of clusters in multidimensional space quite separately from the dimensions onto which those clusters are projected. This is the case with the study here and where there is marked stability in the clustering but dimension labelling is not obvious. We can make chemical and psychological sense of the clustering, however. Recent work in theoretical MDS (Shepard, 1974, Arabie and Boorman, 1973) has abandoned dimensional interpretability in favour of cluster stability as a criterion for accepting scalings.

Observation of the clustering patterns reveals a tendency for molecule type separation (three types of molecules give three separate clusters) and within these

clusters there is a regular pattern dependent on functional groups. There is also a tendency for the more polar stimuli (acetates, ketones, alkenes) to lie to the extremes of the cluster while the less polar stimuli (alcohols, alkanes, epoxides) are grouped at the centre of the cluster.

CHAPTER SEVEN

SORTING EXPERIMENT

The method of sorting (Burton, 1972, 1975) is a data gathering procedure which may be applied to research of this type. This method involves the unconstrained sorting of stimuli by subjects into groups by whatever similarity measure the subjects select. This method may supply additional information to that gathered in the major study (Chapters V and VI).

Rosenberg and co-workers (Rosenberg, Nelson and Vivekananthan, 1968) used the sorting method in a study of the multidimensional structure of personality impressions and their choice of distance function for the solution is of interest here. They suggest that there are two alternative possible ways to represent the psychological relatedness between traits; trait similarity which refers to the synonymity of the two traits, and trait co-occurrence which refers to the degree to which two traits are perceived as occurring in the same situation. It is argued that the trait co-occurrence situation is more appropriate as it is possible for two traits to be grouped together without necessarily being synonymous.

This led them to develop "disagreement scores"

which were obtained by counting the number of subjects who ascribed two traits to two different persons. (In this experiment that would be the assigning of flasks to different groups). The disagreement score for any two traits, i and j, is denoted S_{ij}. The disassociation measure between the two traits (δ_{ij}) was defined as

$$\delta_{ij} = \sum_{k \epsilon T} (S_{ik} - S_{jk})^2$$ where T is the set of traits.

Rosenberg and Kim (1975) have used this formula in the calculation of pseudodistances in a study on kinship terms. In this study they have noted, in reference to sorting tasks:

> "These results indicate that, under certain circumstances, a structure based on single-sort data may not adequately represent the psychological categories and dimensions of a stimulus domain."

They go on to say that:

> "Apparently, respondents tend to ignore a dimension that is extremely obvious when they believe that they have only one opportunity to indicate the dimensions of a set of objects."

If this is the case then one would expect this method to tease out some of the second order effects which are not immediately obvious in the major study's scaling solutions.

Experimental Procedure

Thirty subjects were selected for this study. The subjects had all been participants in the major study so they had prior exposure to the stimuli for this experiment. The subjects were members of Groups III and IV from the major study, there being 17 male and 13 female subjects.

The sorting task required very little time for completion so it was performed, after a short rest period, following the experimental period of the major study. The subjects were issued with instructions (as shown below) and 18 flasks for sorting. These flasks contained the 18 structurally related stimuli used in the previous study. No time limit was imposed for completion of the task but all subjects completed the task in less than 10 minutes.

The instructions to subjects were as follows:

Part B.

> You have been presented with 18 jars containing odorous material. Your task here is to sort these into groups which have similar odour. You may form as many groups as you see fit and each group may contain one or many flasks.
> Do you have any questions relating to this task?

Upon completion of the task subjects left the experimental chamber and the experimenter noted the content of each group sorted.

Analysis

A conversion of cluster content to distances was performed as for Burton (1975) and a matrix of pairwise similarities was generated. Disagreement scores were then generated and Rosenberg and Kim pseudodistances were calculated. The Rosenberg and Kim pseudodistance half matrix was used as input for the POLYCON MDS program.

Two analyses were performed. Firstly a solution was achieved using euclidean metrics and this was found to have moderate stress and linear fit (see below). A city block solution was then performed in an attempt to investigate further the properties of the data. However, the city block solution gave curvilinear fit (disparities on x axis, distances on y axis) and higher stress than the euclidean solution. The city block solution was also found to be less easily interpreted as clusters were not obvious and dimensions uninterpretable.

Results

Five, four and three dimensional solutions were produced for both euclidean and city block metrics. The Table VII-1 below compares the stress values for each of

solutions. These stress values are considerably higher than those achieved in the major study.

Table VII-1

Stress values for the sorting experiment

	Euclidean	City Block
5D	0.490	0.763
4D	0.490	0.751
3D	0.488	0.744
	Linear fit was good for all cases	Linear fit was poor, in all cases curvilinear

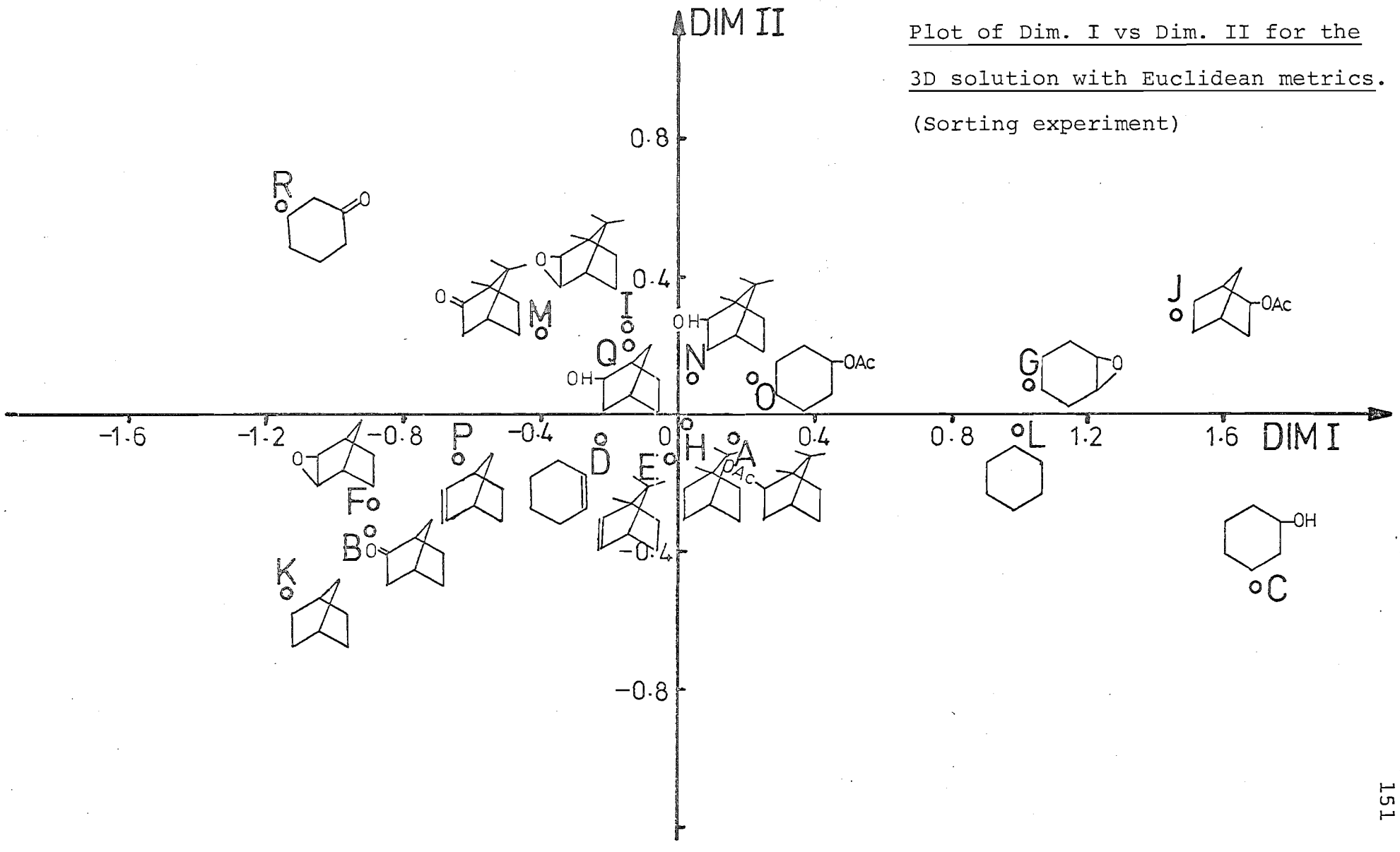
We can see from this table that the euclidean solution is to be preferred. There is very little difference in stress between the 5D, 4D and 3D solutions so the lowest dimensional solution will be considered in the discussion section of this chapter.

The plot VII-1 is a plot of Dim I versus Dim II for the 3D solution with euclidean metrics. This solution has had structural diagrams of the stimuli plotted to assist in interpretation.

Discussion

Interpretation is much more difficult here than for the major study as there is no obvious clustering. This could be partly due to the greater degree of

Plot VII-1



Plot of Dim. I vs Dim. II for the 3D solution with Euclidean metrics.

(Sorting experiment)

variance in the system (higher stress) as a result of the greater flexibility in the task. However, closer inspection reveals that there is some psychological grouping on the basis of chemical functional groups although there is some overlap of these groups in psychological space.

There also appears to be some clustering of molecular types with the bornane derivatives clustered around the origin and norbornane derivatives clustered to the negative side of Dim I and slightly to the negative side of Dim II. However, the cyclohexane derivatives seem to be fairly evenly spread throughout the distribution.

If we now look at the graph VII-1 with regard to functional group positionings we can see some pattern emerging. The ketones and alkenes all lie to the negative side of Dim I and the acetates lie to the positive side of Dim I.

The ketones lie to the negative side of Dim I and are easily seen as a distinct group. This is also the case for the alkenes which lie close to the origin on the Dim II axis. The epoxides tend to lie close to the origin on Dim II and span a considerable range of Dim I. This is also true of the alkanes but they tend to lie slightly to the negative side of the Dim II axis. Two of the alcohols are found close to the origin for both axes and the other alcohol lies to the extreme positive side of the Dim I axis and to the negative side of the Dim II

axis. The acetates all lie on the positive side of the Dim I axis and around the origin on the Dim II axis. Again there is a considerable range of the Dim I axis covered by these stimuli.

Overall there would be some evidence to suggest that the major factor in the distribution of stimuli for this study is functional group type. Once again the acetates tend to lie on the positive side of Dim I and the ketones and alkenes tend to lie to the negative side of Dim I. The Dim II for this study is not interpretable.

Summary

The solutions for the sorting experiment show more stress and have worse linear fit than was the case for the major study. The Rosenberg and Kim suggestion that the subjects ignore the most obvious dimension, or the psychological correlates of some major train of chemical variation (in this case molecule type as seen in the major study) when performing a task of this type, is borne out.

In this case the major determining factor in the distribution appears to be functional group type. This provides information additional to the findings of the major study.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

Multidimensional scaling techniques extract pattern or structure which may otherwise lay hidden in a matrix of empirical data, and represent that structure in a form that is more accessible to the human eye, or more properly to the observer trained to read patterns, that is, as a geometrical model or picture. Objects under study are represented by points in the spatial model in such a way that the geometrical relations among the points reveal the significant features of the data (Shepard, 1972).

Shepard also noted that many MDS solutions reduce to 2 or 3 dimensions which are easily visualizable (Whereas solutions with Factor Analytic techniques tend to be less easily visualized). The interpretation of these MDS solutions may consist of the identification of axes or dimensions, which provides useful information on the basic processes, factors or variables governing the phenomenon under study. Another method of interpretation is a topological or cluster analysis in which consideration is made of the way in which the points gather in particular localities of the scaling solution. This often constitutes the most interpretable aspect of a configuration.

> "Often one may not even know in advance which of these possible structural features of the configuration will be most susceptible to meaningful

> interpretation. In such cases it is clearly hazardous to leave the analysis to any rigidly prespecified analytic method which, necessarily, must rest upon some specific, though perhaps implicit, assumptions about the features to be interpreted. Here again we see the clear advantages of a low-dimensional pictorial representation, in which the investigator can simply look for interpretable features without having to specify in advance exactly what form these must take." (Shepard, 1972).

Multidimensional scaling was selected for the analysis in this study as it provides simple visual patterns of the responses to olfactory stimuli and allows for interpretation of these patterns in relating chemical and psychological variables to perceived odour.

In order to develop an appropirate set of odour stimuli and response scales for the major study of this thesis, a pilot study (Chapter III) and a verbal study of the perceived similarity of word pairs (Chapter IV) was carried out. This study showed observable differences in the responses of subjects to the different molecule types - bornane and norbornane derivatives and functional group types but little variation in responses to three pairs of enantiomers (see plots III-4 and III-5, pp. 72-73). For the major study the series was expanded to include cyclohexane and cyclopentane derivatives and

to include alkanes, acetates and epoxides. Optical enantiomers were not further studied.

The verbal study (Chapter IV) provided appropriate response scale labels, odour words were selected so that they covered a wide section of verbal odour space and were shown to have comparable meaning for all subjects. The odour word space was similar to that found by other authors. In the major study the bornane, norbornane, cyclohexane and anchor compounds were considered using the selected odour words on semantic odour scales.

Nine of the eleven point semantic scales were used for each odour stimulus, with subjects recording their judgements on each of the nine qualities listed (Fig. V-1). These scales are treated as ordinal scales for the input to the POLYCON MDS program. The program is able to generate highly constrained, metric representations using only ordinal data as input. This ability of the newer non-metric methods to extract quantitative metric information from qualitative, non-metric data is suited for work of this type (Shepard, 1972) where the experimenter is not safe in assuming that subjects are treating the response scales as interval or ratio scales. The reliability of the MDS technique used for analysing the data must attain the criteria suggested by Boorman and Arabie (1972) in that the experiments should be reproducible. Responses obtained from the same group of subjects, repeating the experiments, in each case formed comparable solutions.

When the stimuli were presented in the same order to different subjects, closely similar scaling results were obtained. The results obtained were shown to be independent of the order in which the stimuli were presented to them. Thus the scaling solutions were shown to be reliable.

There are no observable differences in the topology of the distributions of the structurally related stimuli both between and within subject groups for the major study. In each scaling solution three clusters of stimuli are observed, namely bornane, norbornane and cyclohexane. Within each cluster some ordering due to functional group is apparent. These topological distributions which were obtained from the scaling solutions, both for and between different groups of subjects, are similar.

The dimension which accounts for the greatest variance of the solutions is Dim. I, a pleasantness dimension, and the remaining dimensions defy definition. Anchor stimuli do not affect the distribution of the structurally related stimuli, which was experimentally attained.

In contrast to the major study, where the molecular structural type was determined to be the major determinant of perceived odour, in the sorting experiment (Chapter VII) this was not as apparent, but the results do show some clustering according to functional group and molecular structure. Rosenberg and

Kim (1975) had earlier reported that in sorting experiments often the most obvious dimension is overlooked by subjects. The results of the sorting experiment confirm the importance of functional group on perceived odour.

While dimensions of odour are difficult to define from both the major study and the sorting experiment, pleasantness is the most easily observed. This compares with Woskow (1968) who studied a variety of odorants and found pleasantness to be the major interpretable dimension and coolness to be a second dimension. Yoshida (1964) in a study of 24 odorants found "resinous-sweet" to be the first dimension and "high pitched-heavy" to be the second dimension. Yoshida did find "pleasantness" to be the major interpretable dimension in two later studies (1972, 1975). Berglund et al (1973) found that an hedonic dimension was the only interpretable dimension, as did Schiffman (1974). All of these studies report difficulty in labelling dimensions. Dimensional interpretations are therefore of limited value and scaling solutions can be more readily interpreted in terms of topology. Most importantly, the topology (e.g. Fig. V-3) seems to be easily interpretable. Arabie and Boorman (1973) and Shepard (1974) have similarly reported that cluster stability is preferable to dimension interpretation for accepting scaling solutions. In the several reported MDS studies of odour quality (see Appendix One) involving very diverse chemical stimuli, topological interpretations have not

been considered and this is perhaps not surprising due to the great variety of chemical stimuli considered.

The major psychological dimension in the parent study, "pleasantness-unpleasantness", was also observed in the verbal study (Chapter IV) where it was linked with a second dimension related to "coolness". It is interesting to note that this parallels the results of Woskow (1968).

Most studies do not consider chemical variations within the cluster of the scaling solutions but this is not the case for the present study which considers this matter. It is not unreasonable with the cluster analysis of the scaling solutions that chemical variations should be able to be isolated within a set of structurally related stimuli.

Amoore's typological approach is not a spatial model. A large number of different odour stimuli are listed under each of the categories and one odour (the primary of that category) is said to be representative of each group. It is difficult to relate Amoore's theory of olfaction to the spatial MDS solutions obtained in this study, because his model limits the odour sensation to a small number of distinct smell types. Amoore's camphoraceous group included cyclohexanol, (1R,2R,4R)-isoborneol and (1R,4R)-camphor. Since all the compounds of this study are similar in "shape" as would be defined by Amoore, we could expect them to fall within the category as being camphoraceous. For Amoore's

theory to be valid we would expect the MDS procedure to give clusters according to his seven or, as he later suggested, thirty-odd primary odour types. It is therefore interesting to note that compounds chosen within one of his odour types can be widely separated in our 2D scaling solutions (Fig. V-3). It is also important to note that the more chemically diverse anchor series is in fact less spread on this grid than the closely related chemical structures.

One cannot escape the observation that Amoore's prediction, that "size" and "shape" are the major odour determinants, is not tenable. If size and shape were dominant it would be expected to be the major dimension in the scaling solution and this is not found.

Wright (1964) suggests radiative excitation is the only form of energy transferred by molecules to the olfactory epithelium.

This energy (vibrational) is attained by a molecule from the kinetic energy of collison between the odorous molecule and the air molecules. From simple energy considerations he concluded that transitions in the infra-red region of about 500 to 50 cm^{-1} were responsible for odour. Wright went on to calculate osmically specific vibrations for both observed spectroscopic frequencies and the more refined normal modes deduced from them (Wright, 1966). Since he was unable to collate this with odour he then went on to consider difference frequencies generated from the normal

modes but these were also unsuccessful in predicting olfactory quality. No attempt was made to measure low infra-red or raman spectra of compounds used in this study.

In the profile-functional group theory (Beets, 1957, 1970) polar groups are considered to be responsible for bonding with receptor sites. For a multifunctional molecule the most polar functional group is considered to be responsible for the orientation of the molecule at the receptor site. Beets' theory differs from Amoore's in its emphasis on functional groups. The results of this study support the proposal that functional group variation is one of the major factors affecting perceived odour quality and in this respect they support Beets' theory. Beets does not suggest that functional groups have odour in their own right but only that they are responsible for the orientation of the odorous molecule with the receptor. He then suggests that "size-shape" of the molecule once bound with the receptor will define smell and at this point the similarity of his ideas with those of Amoore is obvious.

Davies (1953, 1965, 1970) has considered further the effect at the receptor site of odorous molecules and suggested that when they desorb from the lipid cell membrane a sharp hole remains. This implies that the desorption time is short relative to the membrane recovery time and allows Na^+ and K^+ interchange which initiates a nerve impulse. Davies suggests that the

geometry of the odorant and its chemical structure is important in this process. There is some evidence to support these ideas. Desorption at the lipid-water interface has been shown to be related to the cross-sectional area of molecules resulting in clustering according to types such as camphoraceous, floral and musk. Such topological solutions are not dissimilar to those generated in this work. However, one would expect from the results of Davies that the structurally related stimuli in the current study would cluster more tightly than the widely variant anchor stimuli. Davies' experiments do not consider psychological determinants of odour.

Klopping (1971) suggested that functional groups each have their own component odour and he tried to relate the specific odours of certain functional groups to their electronic properties. Our study supports Klopping's theory in as much as some systematic variation is shown within the structural classes of compounds as the functional groups are changed, as well as systematic variation with molecule type.

We see, overall, that the results of the current study demonstrate just how complex the problem of odour quality determination is. The use of structurally related stimuli, to limit the chemical variation in a stimulus set, allows for greater certainty in attributing chemical determinants of perceived odour. The variety of odiferous compounds is almost as vast as the variety

of chemical substances, suggesting unlimited research possibilities and pointing out the need for judicious choice of experiments. Clearly, however, the experimental methods used and developed for this work can be usefully employed in gaining further insight into what is a very difficult and important problem.

APPENDIX ONE

Yoshida M. Japanese Psychological Research, 6, 145-154, 1964. "Studies of Psychometric Classification of Odors (5)."

Stimuli Used

Representative odours were selected by Kainoshow according to his own scheme. His scheme is based on twenty years experience as a perfumer and was presented at meetings of organoleptic testing sponsored by J.U.S.E. These 24 odorants were from a variety of odour types with the exception that very repugnant odours were not included.

Method of Presentation

No mention of the exact method of presentation is recorded but it is stated that the subjects were asked to smell odours of dilute solution. No mention is made of the solvent(s) used.

Method of Eliciting Judgement

Three experiments were included in this paper; the method of judgement varied with the experiments.

For the first experiment (Expt. VI) multidimensional scaling based on direct estimation of similarity was used. The number of categories of similarity judgement was 5, that labelled 1 being the most dissimilar and 5 being most similar.

No mention is made of the method of judgements (e.g. all pairwise comparisons, randomised). An indica-

tion that more than one judgement was made for each pair of stimuli is seen in that intra-individual consistency is quoted as being fairly high. Inter-individual agreement was not so good and the results for the 6 naive subjects were discarded. The results obtained from the 2 perfumers was used in the MDS.

For the second of the experiments (Expt. VII) it was desired to establish semantic differential scales of odours. It was thought desirable to describe in advance some of the qualities of each stimulus in order to facilitate the interpretation of factors. A battery of 25 such scales was constructed and thirty subjects rated 44 stimuli which had been used previously (Expt. V and VI). Samples were selected from a wide range of materials. It was suggested that it is far easier to describe the odours in this way than to judge directly the similarity for each pair of stimuli and that this would lead to higher values of the reliability of judgements. The types of scales which were used include: pleasant-unpleasant, clear-dirty, narcotic-stimulating, sweet-sour. A correlation matrix was set up and Thurstone's multiple factor analysis was applied to the correlation matrix. Seven point bipolar scales were used.

For the final experiment (Expt. VIII) monopolar scales were used, this method being proposed due to the difficulty in finding pairs of adjectives with exactly opposite meanings. Yoshida selected 20 adjectives and

used 25 female students as subjects, the same 44 stimuli were used as in the previous experiment. He used a 5 point monopolar scale and correlation matrix followed by factor analysis was used as for Expt. VII.

Type of Rating Scale

Expt. VI	5 point interval scale
Expt. VII	7 point scale
Expt. VIII	5 point scale.

Method of Converting ratings to input of MDS or other model

This was not noted for Expt. VI but this may be written up more fully in Expt. V which is in a previous paper. This has been previously noted under Method of Eliciting Judgement for Expt. VII and Expt. VIII.

Interpretation

Expt. VI. Of the six factors extracted, three were regarded as real. The first factor is said to obviously be resinous versus sweet. The second factor seemed to be an apposition of high pitched note versus heavy note and the third factor was not clear.

Note: Only two subjects were used and very repugnant odours were not used in the experiments. No comparisons were made of the individual odour spaces of the two subjects (both of whom are perfumers). Naive subjects were said to have responded predominantly on a Pleasantness-Unpleasantness dimension.

Expt. VII. Three factors were extracted.
(i) "dynamism magnitude" or "sensory pleasure",

(ii) "harsness",

(iii) "intensity" or "vividness" factor.

Expt. VIII. Ratings by naive subjects were limited to scales not emphasized by the specialists when comparing the interaction between scales and subjects. There is a suggestion that this may be due to poorness of vocabulary of the naive subjects. Dimension (i) "sensory pleasure", (ii) "harsness", (iii) "vividness" factor of Expt. VII expressed as "persistent".

Yoshida, M. Japanese Psychological Research, 14, 70-86. 1972. "Studies in Psychometric Classification of Odors (6)."

Stimuli Used

Two experiments were reported in this paper. Expt. I was a re-analysis of Amoore's theory of olfaction and Expt. II was a re-analysis of Dravniek's similarity experiment. In Expt. I 96 of the 108 compounds used by Amoore and Venstrom (1967) were used. These were representative of each of the seven odour categories used by Amoore. In a second part of Expt. I, 28 of these 96 were chosen and an R technique analysis was performed where additional electrophysiological data were available (Takagi et al, 1969).

In Expt. II, 21 odours were used as in Dravniek's work (1967, 1971). These 21 odours were chosen as varying in a variety of physical properties such as boiling point, vapour pressure, refraction, hydrogen

bonding and molecular weight. Three different MDS methods were used in the analysis.

Method of Presentation

No method of odour presentation is recorded for either Expt. I or Expt. II.

Method of Eliciting Judgement

Rating scales were of 9 points for Expt. I with 0 being the least similar and 8 being the most similar. No mention is made of the number or type of subjects used and no mention is made of the number of times each stimulus pair was presented for judgement per subject. An eight point scale was used for Expt. II but no reason was offered for this choice. The type of rating scale was as in Expt. I with 0 being no similarity and 7 being complete similarity.

Method of Converting ratings to input of MDS or other model

For Expt. I, two different types of Principle Components Analysis were used. The first was a PCA of the correlation matrix among odours (Q technique on the stimulus space), while the other was a PCA of the correlation matrix among scales (R technique on the chemical and organoleptic scale space).

Expt. II. Three types of analyses were used on the original data: Torgerson's distance model of MDS, Ekman's model of MDS (a version of Hayashi's qualification method) and Micko's extension of Ekman type MDS.

Since the original data are based on distance

judgements, the first type seems to be more pertinent. Input scores seem to have been grouped and averaged over subjects and then scaled onto a distance measure, being equivalent to the original judgement scale.

Interpretation

Expt. I. The first 3 or 4 factors are enough to account for the original data matrix. Interpretation of factors is not easy. The first factor is not easily interpretable although it has a very large Eigenvalue. Gregson (1972) also found the same tendency when using non-metric functioning of Coomb's type. The PCA of type Q and 12 variables showed "ethereal" to be positive on Dim. II and musky, minty negative for the third dimension. The positive side of the fourth represents musky and the negative side minty. Spicy may be the best representative of the first axis.

The PCA of type Q on 7 variables showed spicy (I) and camphorous (II). Yoshida concludes that Amoore's standard chemicals are not necessarily the most representative ones, and do not provide clues enough for the interpretation of axes.

The PCA R technique gave a first axis which was not hedonic tone but had floral, musky, minty and camphoraceous on the negative side and ethereal, putric and pungent on the positive side. The second factor is labelled (cool-harsh) versus (warm-soft) and the third is (heavy) versus (light).

Yoshida concluded that Amoore's primaries may be

reduced to four; (floral, musky), (minty, camphoraceous), (pungent, putrid), and (ethereal).

Expt. II. A summary of the dimension labels is as follows:

(A) Torgerson's MDS. Dim. I - pleasant - unpleasant
Dim. II - not easily named
Dim.III - not easily named
Dim. IV - not easily named

(B) Ekman-Hayashi MDS.Dim. I - not easily named
Dim. II - foul, burnt - unsure
Dim.III - not easily named

(C) Micko's halo model.
Dim.I-IV - not easily named.

Yoshida, M. Chemical Senses and Flavour 1, 443-464, 1975. "Psychometric Classification of Odours."

Stimuli Used

Standard test odours were selected from the works of Amoore, Schutz, Wright and Michels, and Takagi. These included Amoore's seven "primary odours" (1967), seven of the eight proposed by Wright and Michels (1964), all nine of the standards of Schutz (1964) and all ten of the odorants proposed by Takagi (1971). In addition 36 essential oils of varying quality were used.

Method of Presentation

Stimuli were presented on blotting paper after solvents had been evaporated.

Method of Eliciting Judgement and Type of Rating Scale

A similarity scale of 9 points was used. Zero represented no similarity at all and 8 represented the most similar.

Method of Converting ratings to input of MDS or other model

Both PCA and MDS were carried out. For the PCA the data matrix of the average ratings from 20 subjects was used directly for the factor analysis.

Two distance matrices were constructed for the MDS. One was based on the city block model and the other on the euclidean space model. Both Torgerson and Kruskal type MDS were performed for each case.

Interpretation

Using Torgerson's metric the Dim. I versus Dim. II solution for both city block and euclidean cases yields essentially the same solution. On the positive side of the first axis are pleasant odours and on the negative side are unpleasant odours. The labelling of the second axis is not clear. The standards of Amoore cluster most narrowly while those of Wright-Michels scatter most widely.

Kruskal's MDS allows for 4 cases. Euclidean distance - euclidean processing, euclidean distance - city block processing, city block distance - city block processing, and city block distance - euclidean processing. The euclidean - euclidean case yields a solution with the lowest stress. There is some suggestion with this

solution that Dim. I is hedonic and Dim. II is resinous - non-resinous. Higher dimensionality solutions up to Dim. X are noted. PCA solutions are not mentioned in this summary as they are not directly relevant to this thesis.

Berglund, B., Berglund, U., Engen, T. and Ekman, G. Scandinavian Journal of Psychology, 14, 131-137, 1973. "Multidimensional Analysis of Twenty-one odors."

Stimuli Used

The odorants were selected to vary as much as possible in retention time and pleasantness. This was chosen as a result of work by Mozell (1970) who showed correlations between retention times and physiological data. Another basis for choice of odorants was related to pleasantness which was shown by Woskow (1968) and Engen and McBurney (1964) to be an important determining factor.

On the basis of the subjective scales of odour intensity from the previous study (Berglund et al, 1971) the 21 odorants were matched in subjective intensity by the same subjects who served in both experiments. The odorants which were used represent large variations in molecular weight, vapour pressure at 20^{o}C, chemical structure, retention time and solubility in polar and non-polar substances.

Method of Presentation

The liquid odorants were presented in pairs to

each subject on a cotton wad saturated with the odorant and kept in a standard sized test tube. The diluent in most cases was diethylphthalate.

Method of Eliciting Judgement

The subject's task was to estimate the qualitative similarity of the odours in each pair. These estimates were given according to a percentage scale in which 0 represents "no similarity" and 100 "identity". Previous methodological studies have shown that the judgements obtained by this method can be considered as ratio estimates (Ekman and Waern, 1959, Ekman et al, 1964).

Type of Rating Scale

0 representing "no similarity" to 100 representing "identity".

Method of Converting ratings to input of MDS or other model

A matrix of similarity judgements was achieved by computing the arithmetic mean of the four judgements of each pair of odorants. Pearson's product-moment correlation was then calculated on the two similarity matrices for all possible pairs of subjects.

The vector model of Ekman (1963) was chosen for this analysis and transformation of the similarity values into cosine values was made according to that model. The transformation was made separately for individual and group means. In analysing the cosine matrices, a component analysis with the method of principle components was used.

Interpretation

There is some indication that different individuals have different odour spaces (there was a low correlation among individual similarity matrices). Comparison of the factor loadings obtained in the component analysis supports the notion that different individuals have different odour spaces. Eight of the eleven subjects were found to have a hedonic dimension but interindividual differences appear large both in ranking pleasantness and in judging similarity.

It was not possible to establish the existence of a dimension related to retention time. This may be the result of the variability of the data. Dimension labelling was not attempted but a table is presented which shows the total number of factors extracted and the proportion of variance explained as well as designating which of the factors is hedonic and the proportion of the variance attributed to the hedonic factor.

Schiffman, S.S. Science, 185, 112-117, 1974.
"Physicochemical Correlates of Olfactory Quality."

Stimuli Used

This study reanalysed data collected by Wright and Michels (1964) and Woskow (1964). The Wright and Michels study compared 50 olfactory stimuli (5 were duplications) with 9 odorant standards which ranged widely in quality. Woskow (1964, 1968) used 25 olfactory stimuli of varying odour quality.

Method of Presentation

Stimuli were presented in 30 ml wide mouthed reagent bottles containing the test substance in unadulterated form as for Woskow (1964). One exception was that of acetic acid which was a 20% solution with water.

Method of Eliciting Judgement and Type of Rating Scale

The required verbal judgements were made on a 9 point scale where one indicated "most alike" and nine indicated that the two odours were "dissimilar".

Method of Converting ratings to input of MDS or other model

For the Wright and Michels study the 50 odorants were taken and correlated across the standards with the assumption that odorants having similar smell quality would be highly correlated. The 50 by 50 correlation matrix was factor analysed by Wright and Michels and 8 factors were obtained. In this study the correlation matrix was reanalysed according to Guttman's general non-metric MDS technique.

In his initial work Woskow used an MDS with metric assumptions and found 3 dimensions accounting for 80% of the variance. These data were reanalysed by the non-metric technique of Guttman. This resulted in a 2 dimensional solution which accounts for 84% of the variance.

Interpretation

The two dimensional solutions achieved by appli-

cation of Guttman's MDS procedure to both sets of data are somewhat similar. The spaces for both consist of two groups, a more pleasant group and a more unpleasant group. The stimuli used in common fall at closely analogous points.

> "The similarity of these two solutions, each obtained from different numbers of stimuli and by different psychophysical techniques, leads me to conclude that a 2 dimensional space adequately describes the relationship among a wide range of olfactory stimuli" (Schiffman, 1974).

It was impossible to make any conclusion about the stereochemical properties with regard to determining olfactory quality. Scale models were built for some of the compounds and Amoore's theory was not confirmed.

Functional groups, however, were found to be good distinguishing factors for olfactory quality. Other aspects for which some degree of association was observed were molecular weight and boiling point of the substances. There were no trends for freezing point, solubility in water, dipole moment and the number of double bonds in the stimuli. Some support was found for Wright's theory with correlations of Raman frequencies being associated with pleasantness and unpleasantness.

Woskow, M.H. Theories of odour and odour measurement, 147-191, Istanbul (1968). Ed. N. Tanolac.
"Multidimensional Scaling of Odours."

Stimuli Used

Twenty-five odorants were used. These were of varying pleasantness but no statement has been made of the selection criteria.

Method of Presentation

Sniff bottles were 30 ml with wide mouthed ground glass stoppers. All odorants were unadulterated with the exception of acetic acid which was made up to be a 20% solution with distilled water. A random order of presentation of pairs of stimuli was used.

Method of Eliciting Judgement and Type of Rating Scale

Verbal judgements were made on a 9 point scale where one indicated "most alike" and nine indicated that the two odours were "dissimilar". The numbers between 1 and 9 were to be taken as indicating degrees of difference between the extremes.

Method of Converting ratings to input of MDS or other model

Data were scaled onto distances by the equal appearing interval model which involved taking the mean category value for each stimulus pair (i.e. the mean of 20 category judgements). These were then converted to a matrix of scalar products using Torgerson's formula.

Interpretation

Judgements were made of the pleasantness of each of the stimuli in addition to this experiment. The relation of the judged pleasantness of the odours to their position along the Dim. I axis suggests that Dim. I

represents pleasantness.

The second dimension was characterised by high loadings for menthol, camphor, pinene and guaiacol. It was suggested that this dimension was a "coolness" or "woodiness" dimension.

The third dimension defied interpretation.

Gregson, R.A.M. and Mitchell, M.J. Chemical Senses and Flavour 1, 95-101, 1974. "Odour Quality Similarity Scaling and Odour-word Profile Matching."

Stimuli Used

Seven odorants were chosen for their diversity of odour quality. Some had been suggested as primary odours by other investigators.

Method of Presentation

The odorants were kept in 100 ml ground glass stoppered bottles in solid and liquid form as supplied. No attempts were made to match for intensity or to control for purity. All substances were undiluted.

Method of Eliciting Judgement and Type of Rating Scale

Pairwise similarity ratings were made over all possible pairs in a randomised sequence. The scale used was an 11 point scale running from "0" (completely different) to "10" (identical). Part (ii) of this study used odour words as well as odour stimuli.

Method of Converting ratings to input of MDS or other model

INDSCAL (Carroll and Chang, 1970) was chosen for

this study and raw similarity judgements were used as input to INDSCAL.

Interpretation

The major point of the study was to show that MDS methods are vulnerable to verbal labelling factors or processes. That is, there are similarities between odours, similarities between words and similarities between odour names.

A three dimensional solution was selected for part (i) of the study and this accounted for 56% of the variance. No dimension labelling was attempted with such a small number of stimuli. This study has been included in this appendix primarily because it uses the INDSCAL program for analysis of an odour stimuli task. The study is not concerned primarily with classification of odour quality.

APPENDIX TWO

STEREO VIEWS OF PLOTS FROM CHAPTERS 5 AND 6.

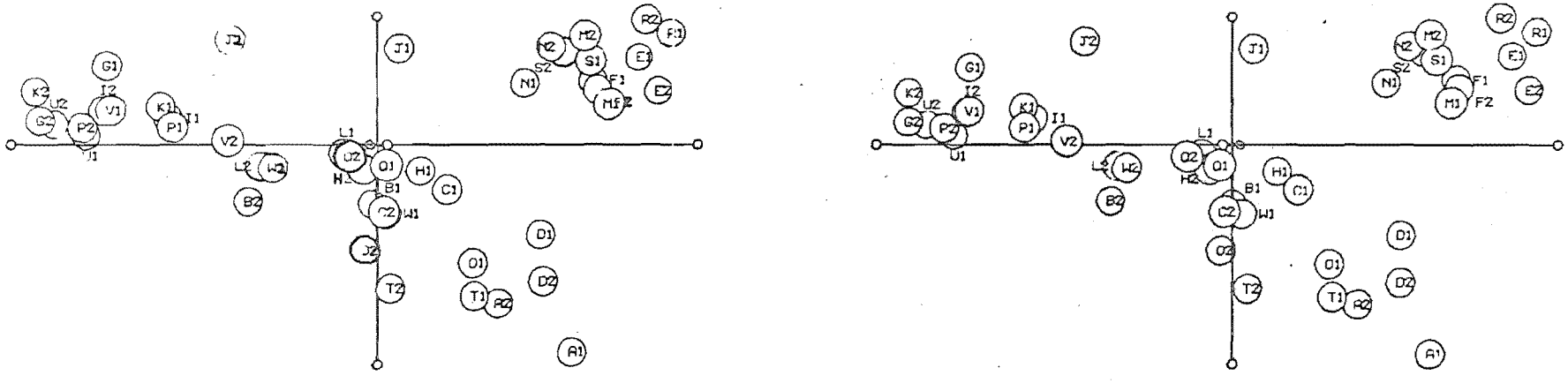
A set of large stereo views is included for use with a large stereoscope. The smaller views are for use with stereo viewers supplied by Taylor-Merchant Corporation with 13.5 cm focal length.

No obvious trends emerge for the distributions along the third axes.

NOMENCLATURE FOR USE IN GRAPHING. MAJOR STUDY. (Stimuli)

	GROUP I		GROUP II		GROUP III		GROUP IV	
	Pre 1	Pre 2	Pre 1	Pre 2	Pre 1	Pre 2	Pre 1	Pre 2
Isoamylacetate	A1	A2		A4			A7	A8
Methylpropionate	B1	B2		B4			B7	B8
n-Propanol	C1	C2		C4			C7	C8
Eugenol	D1	D2		D4			D7	D8
1,6 Cineole	E1	E2		E4			E7	E8
(1R,2R,4R)-Born-2-yl acetate	F1	F2	F3	F4	F5	F6		
Norcamphor	G1	G2	G3	G4	G5	G6		
Cyclohexanol	H1	H2	H3	H4	H5	H6		
Cyclohexene	I1	I2	I3	I4	I5	I6		
(1R,4R)-Born-2-ene	J1	J2	J3	J4	J5	J6		
2,3exoEpoxynorbornane	K1	K2	K3	K4	K5	K6		
Epoxycyclohexane	L1	L2	L3	L4	L5	L6		
Bornane	M1	M2	M3	M4	M5	M6		
(1R,2S,3R,4S)-2,3-Epoxybornane	N1	N2	N3	N4	N5	N6		
exo-Norborn-2-yl acetate	O1	O2	O3	O4	O5	O6		
Norbornane	P1	P2	P3	P4	P5	P6		
Cyclohexane	Q1	Q2	Q3	Q4	Q5	Q6		
(1R,4R)-Camphor	R1	R2	R3	R4	R5	R6		
(1R,2R,4R)-Bornan-2-ol	S1	S2	S3	S4	S5	S6		
Cyclohexylacetate	T1	T2	T3	T4	T5	T6		
Norborn-2-ene	U1	U2	U3	U4	U5	U6		
exo-Norbornan-2-ol	V1	V2	V3	V4	V5	V6		
Cyclohexanone	W1	W2	W3	W4	W5	W6		

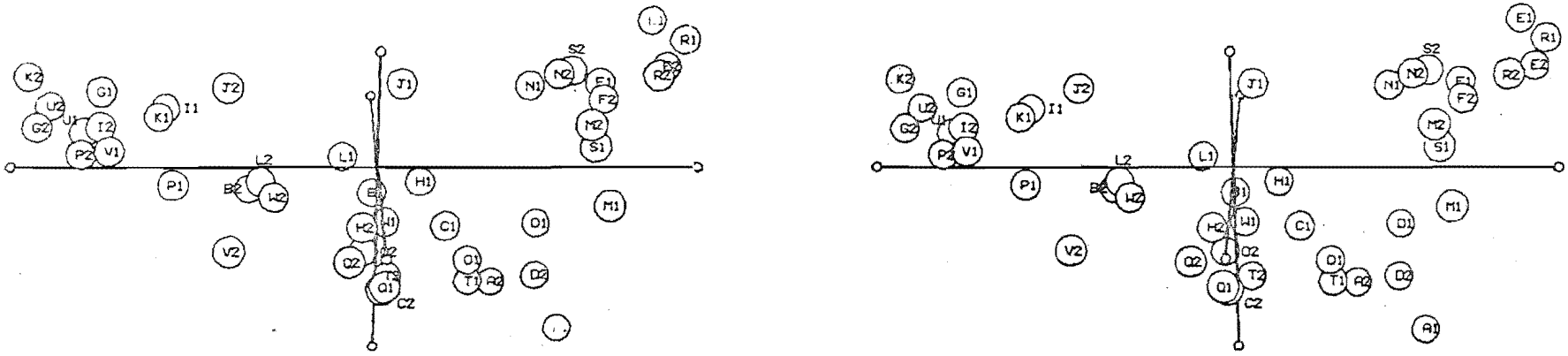
GRAPH 2-1



GROUP I

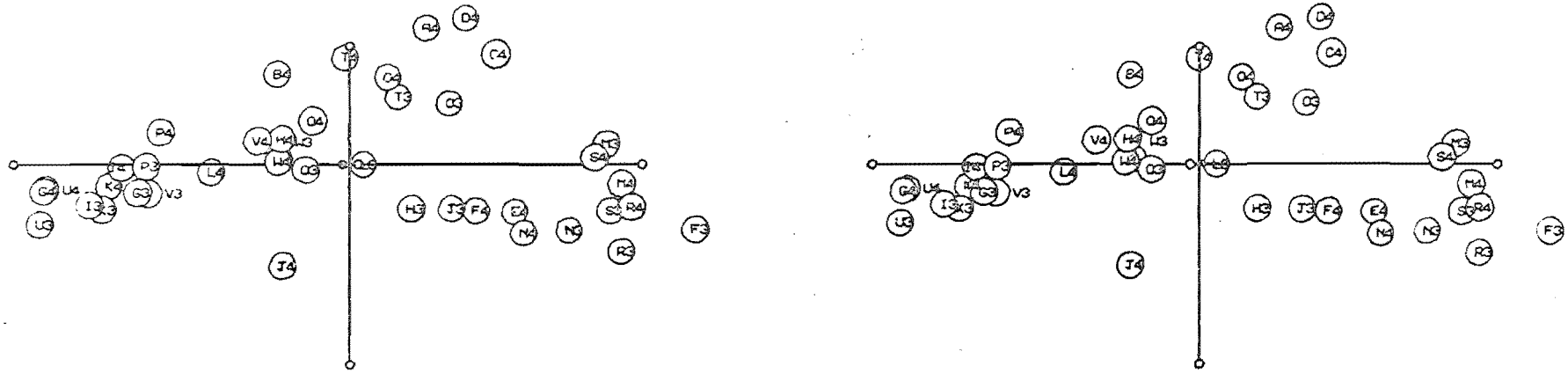
PRESENTATION 1 vs PRESENTATION 2

GRAPH 2-2



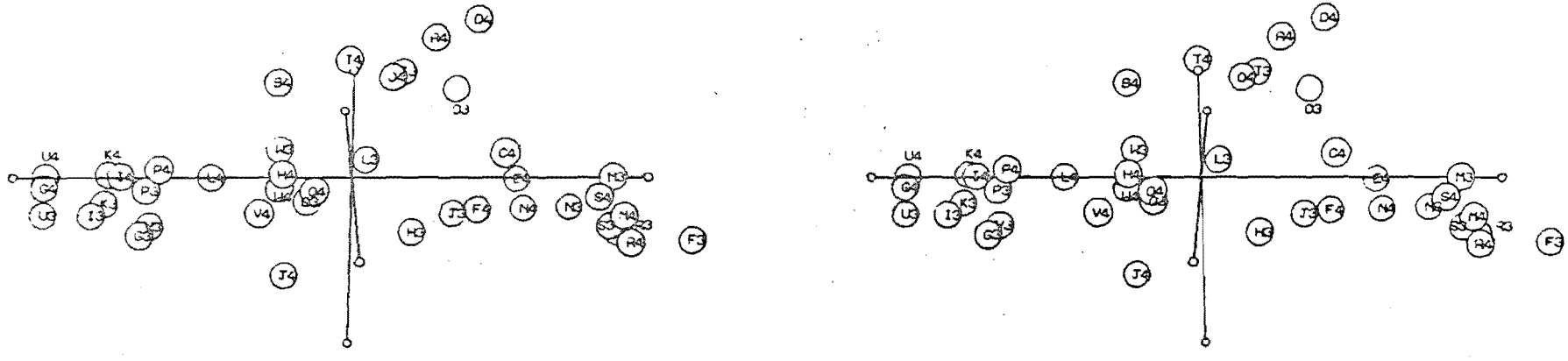
GROUP I, PRESENTATION 1 vs PRESENTATION 2, 30° ROTATION

GRAPH 2-3



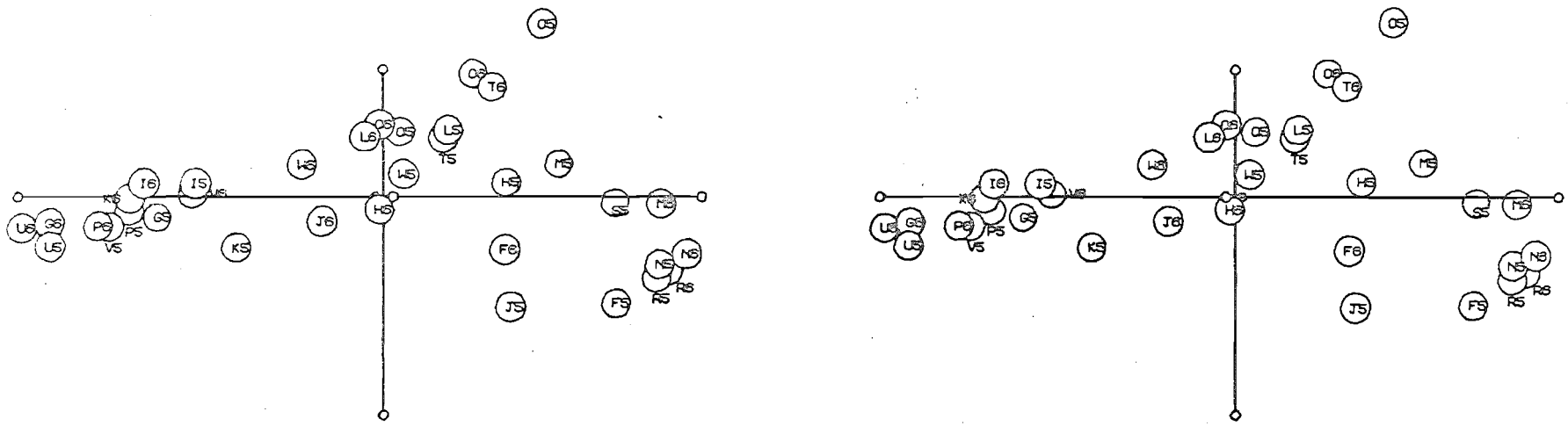
GROUP II, PRESENTATION 1 vs PRESENTATION 2

GRAPH 2-4



GROUP II, PRESENTATION 1 vs PRESENTATION 2, 30° ROTATION.

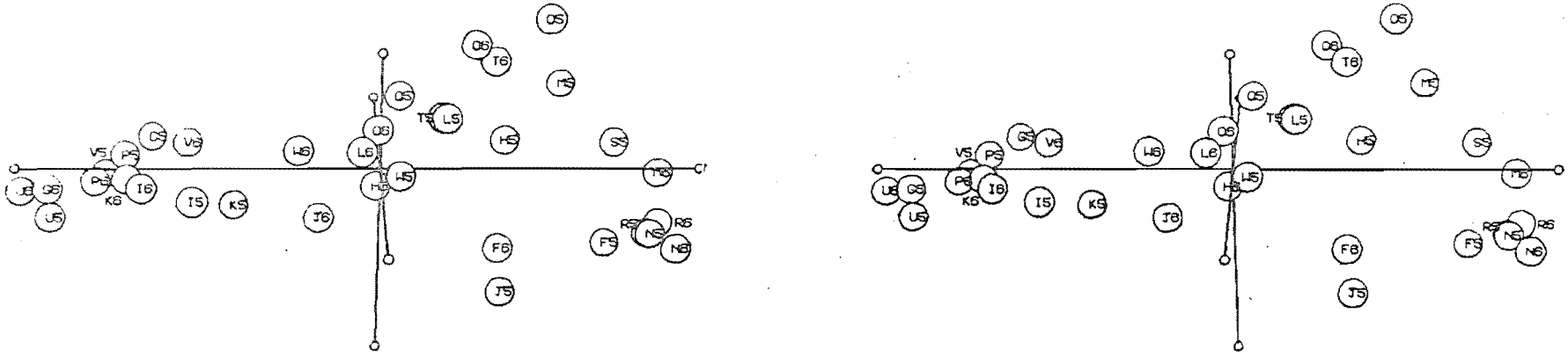
GRAPH 2-5



GROUP III

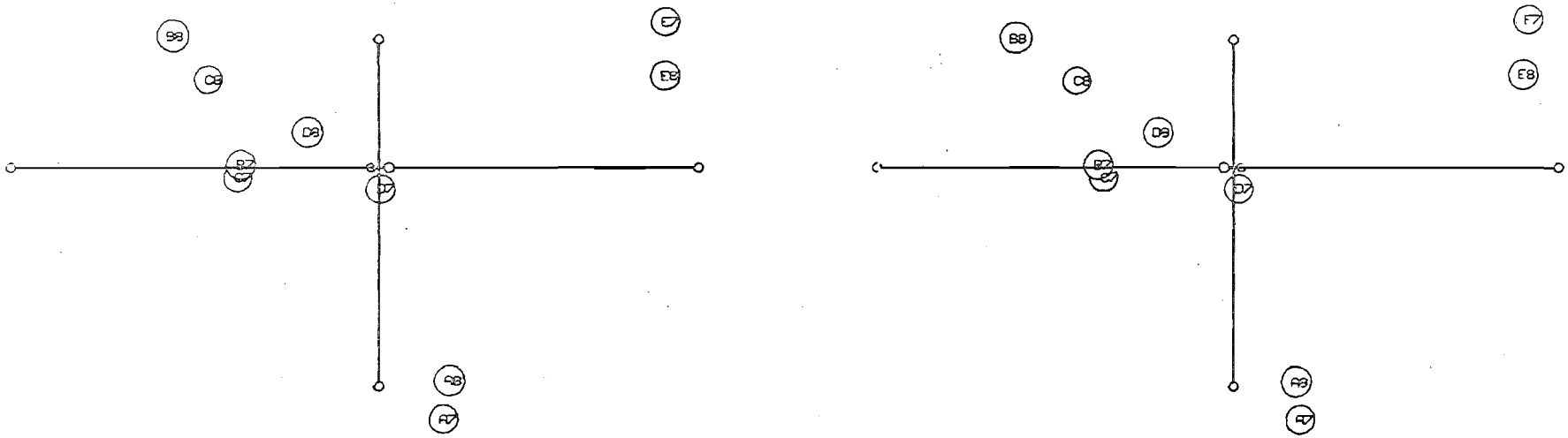
PRESENTATION 1 vs PRESENTATION 2

GRAPH 2-6



GROUP III PRESENTATION 1 vs PRESENTATION 2, 30° ROTATION

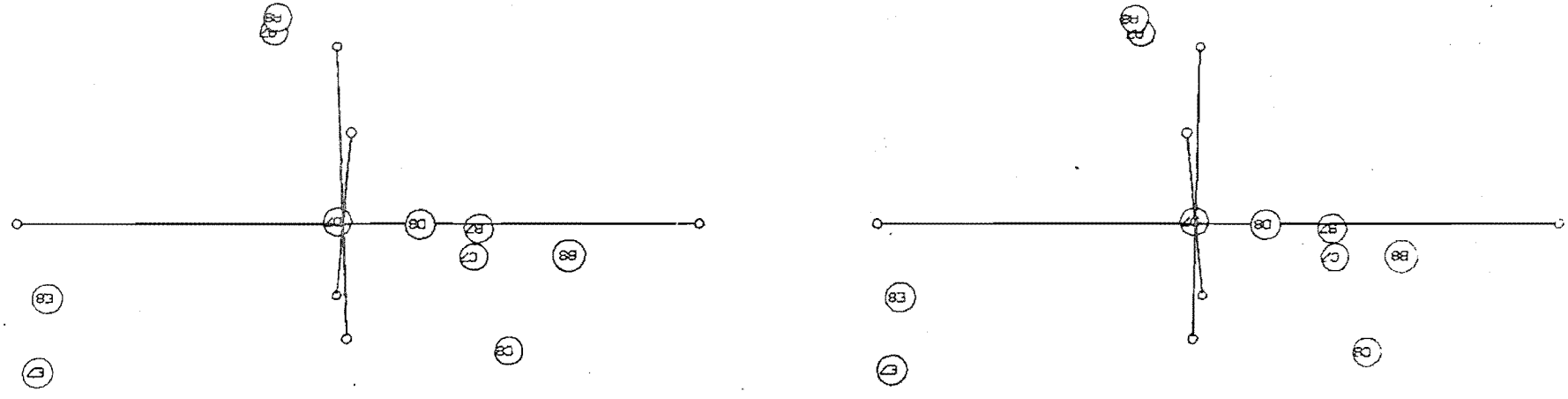
GRAPH 2-7



GROUP IV

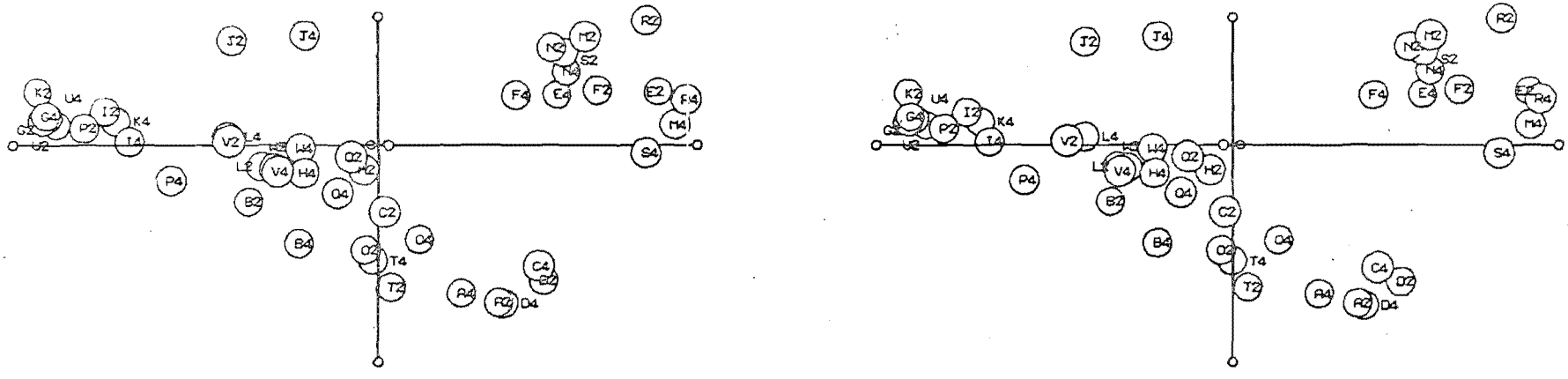
PRESENTATION 1 vs PRESENTATION 2

GRAPH 2-8



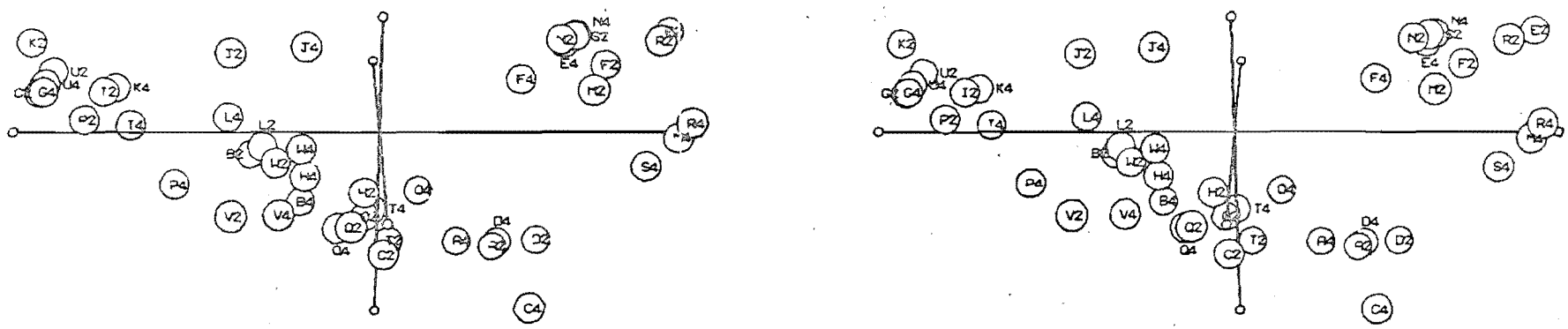
GROUP IV PRESENTATION 1 vs PRESENTATION 2, 30° ROTATION

GRAPH 2-9



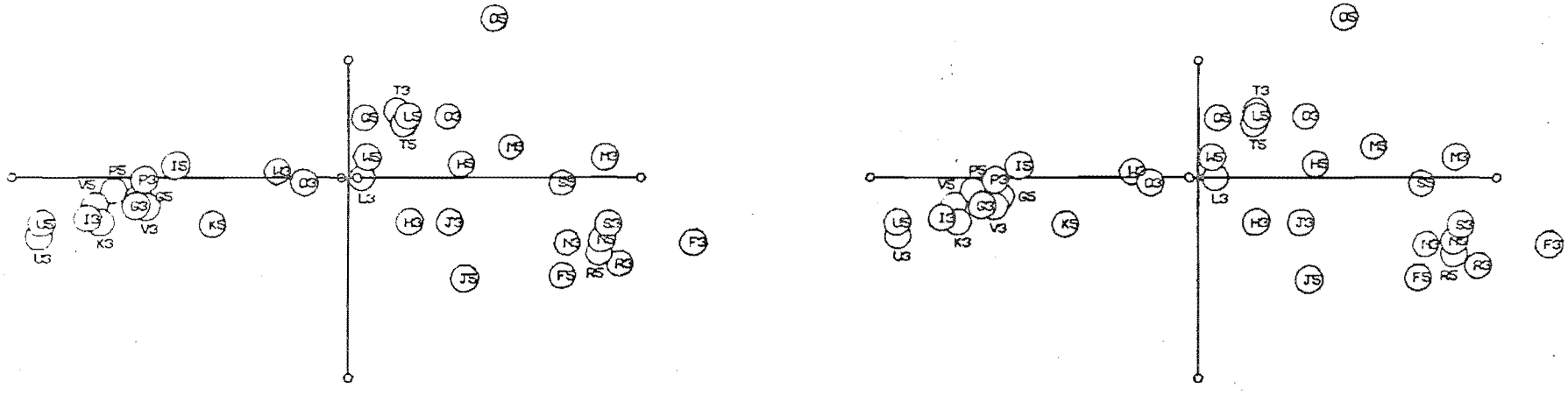
GROUP I, PRESENTATION 2 vs
GROUP II, PRESENTATION 2

GRAPH 2-10



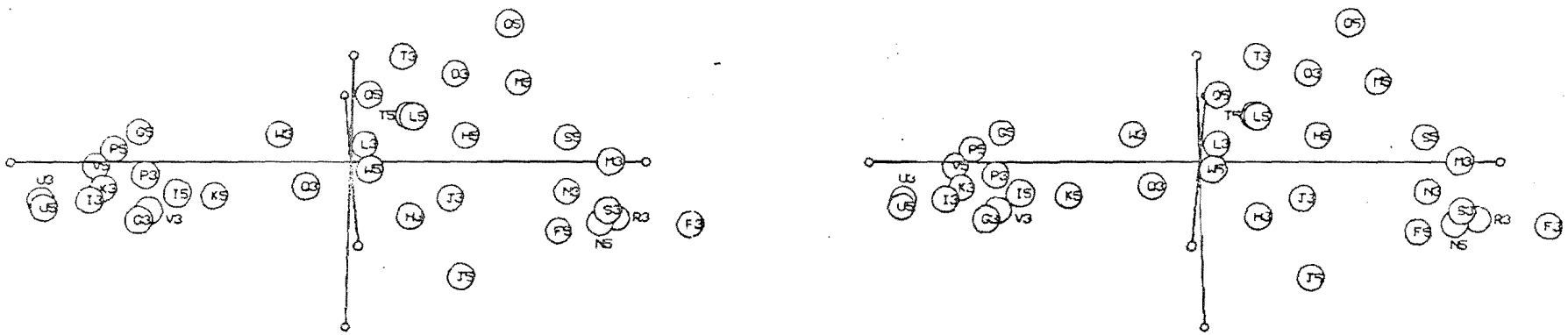
GROUP I, PRESENTATION 2 vs
GROUP II, PRESENTATION 2, 30° ROTATION

GRAPH 2-11

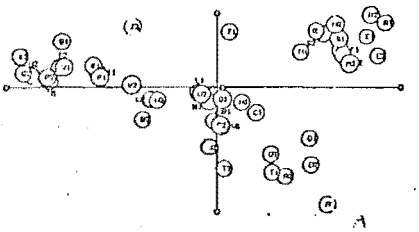


GROUP II, PRESENTATION 1 vs
GROUP III, PRESENTATION 1.

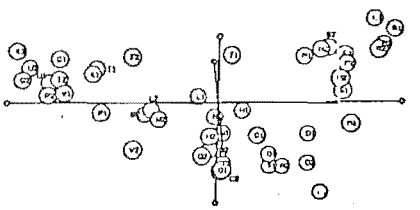
GRAPH 2-12



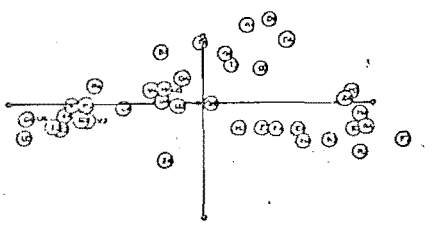
GROUP II, PRESENTATION 1 vs
GROUP III, PRESENTATION 1, 30° ROTATION



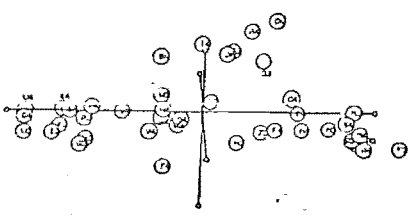
Graph 2-1
Group I
Presentation 1
vs
Presentation 2



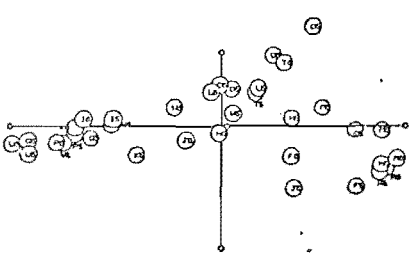
Graph 2-2
Group I
Presentation 1
vs
Presentation 2,
30° Rotation



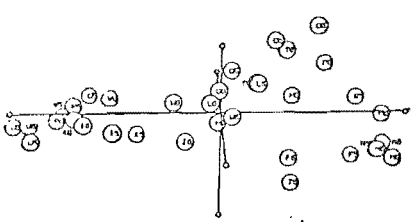
Graph 2-3
Group II
Presentation 1
vs
Presentation 2



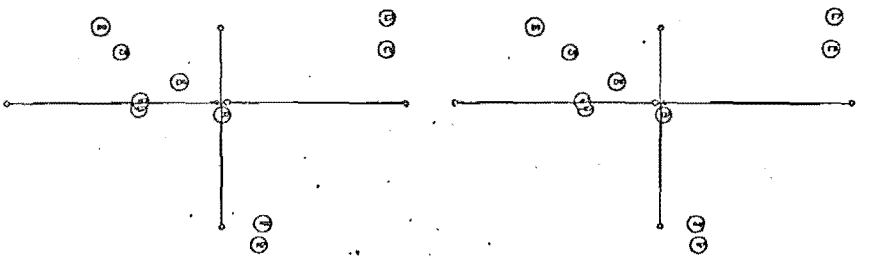
Graph 2-4
Group II
Presentation 1
vs
Presentation 2,
30° Rotation



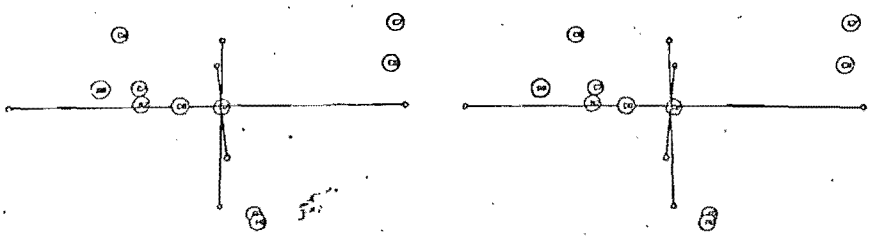
Graph 2-5
Group III
Presentation 1
vs
Presentation 2



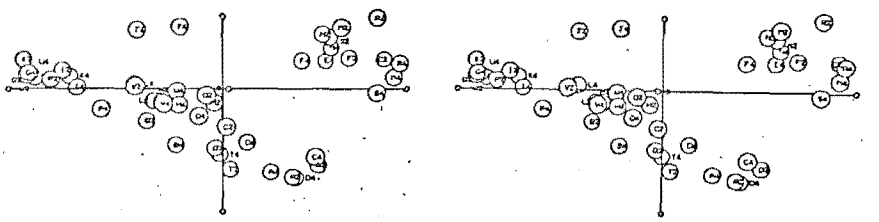
Graph 2-6
Group III
Presentation 1
vs
Presentation 2,
30° Rotation



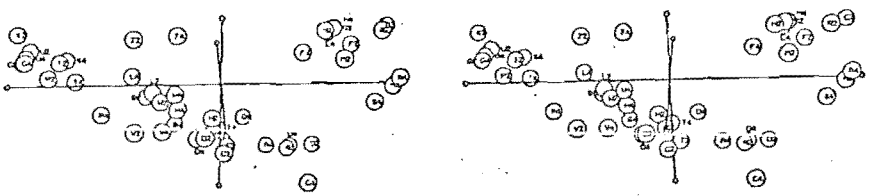
Graph 2-7
Group IV
Presentation 1
vs
Presentation 2



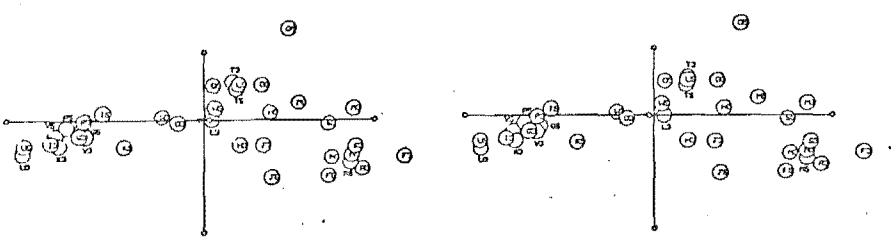
Graph 2-8
Group IV
Presentation 1
vs
Presentation 2,
30° Rotation



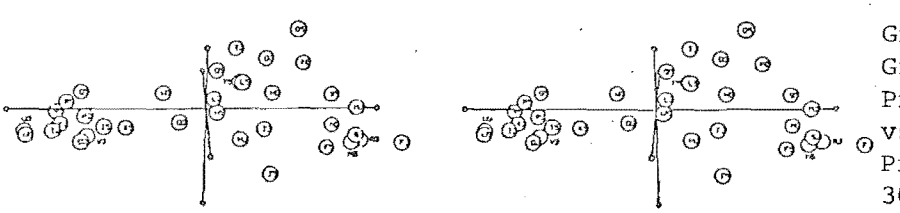
Graph 2-9
Group I
Presentation 2
vs Group II
Presentation 2



Graph 2-10
Group I
Presentation 2
vs Group II
Presentation 2,
30° Rotation



Graph 2-11
Group II
Presentation 1
vs Group III
Presentation 1



Graph 2-12
Group II
Presentation 1
vs Group III
Presentation 1,
30° Rotation

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